HIGH NITROGEN EXPLOSIVES. PART 2.   DIBENZO-1,3a,4,6a-TETRAAZAPENTALENES   AND BENZO-1,2,3,4-TETRAZINE-1,3-DIOXIDES

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AUGUST 1996

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FOREWORD

The continuing Navy requirement for dense, powerful but insensitive explosive and propellant ingredients may be satisfied by synthesis of new high nitrogen materials. This report documents research towards the synthesis and characterization of dibenzo-1,3a,4,6a-tetraazapentalenes and benzo-1,2,3,4-tetrazine-1,3-dioxides. Part 1 of this report was published as NAWCWPNS TP 8211 in September 1994.

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12 August 1996

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Released for publication by
S. HAALAND
Director for Research & Engineering

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE August 1996	3. REPORT TYPE AND DATES COVERED Progress, Feb 94-Jun 95

4. TITLE AND SUBTITLE
High Nitrogen Explosives. Part 2. Dibenzo-1,3a,4,6a-tetraazapentalenes and Benzo-1,2,3,4-tetrazine-1,3-dioxides

6. AUTHORS
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5. FUNDING NUMBERS
PE 61153N
Project R2402, R2502
Task R2402, R2502
Work Unit 113570

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Naval Air Warfare Center Weapons Division
China Lake, CA 93555-6100

8. PERFORMING ORGANIZATION REPORT NUMBER
NAWCWPNS TP 8277

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy
Arlington, VA 22207-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION /AVAILABILITY STATEMENT
A Statement; public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

(U) High nitrogen materials are sought as a potentially dense, powerful but insensitive explosive and propellant ingredients. Elucidation of the structure and chemistry of dibenzo-1,3a,4,6a-tetraaza-pentalenes has continued, with particular attention to a putative $C_{12}N_{12}O_{12}$ derivative initially prepared at the University of New Orleans. This research contributed substantially to identification of the actual *o*-quinone hydrate structure, and explanation of the apparently anomalous explosive insensitivity of the material. Synthesis of the novel 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide has been repeated, its structure has been confirmed, and preliminary evaluation of its explosive sensitivity has been completed.

14. SUBJECT TERMS
Explosives, Synthesis, Sensitivity, Stability, Performance

15. NUMBER OF PAGES
58

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	**UNCLASSIFIED**	**UNCLASSIFIED**	**UL**

CONTENTS

ACKNOWLEDGMENTS

INTRODUCTION

The Navy's ongoing requirement for energetic materials of superior performance, both as explosives and as propellants, is well documented. Such ingredients are required to enable missile systems to defeat more demanding targets at longer range, and productive programs have led to the synthesis and development of new dense energetic materials with enhanced performance as explosives and/or propellant oxidizers, such as hexanitrobenzene, CL-20, polynitrocubanes and ammonium dinitramide (ADN) (Reference 1).

There is a parallel need for new insensitive energetic materials, both to reduce the hazards of accidental initiation in response to inadvertent stimuli or enemy action, and to withstand the rigors of impact on, or penetration of, a hardened target but still function as intended. This reduction in sensitivity must of course be achieved without impairing the performance of the missile system, and there is, therefore, a specific requirement for materials with the performance of cyclotrimethylenetrinitramine (RDX) (**1**), as reflected in its detonation velocity and pressure, and the explosive insensitivity and chemical stability of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (**2**). Throughout this report detonation parameters quoted are those calculated using the empirical predictive formulae of Rothstein and Petersen (Reference 2), while densities are those obtained using the group additivity method of Holden (Reference 3). Experimental densities, where known, are given in parentheses. These simple methods require input of no experimental data, and as such are well-suited to estimation of properties of proposed target molecules yet to be prepared. However, neither is sufficiently sophisticated to account for polymorphism, isomerism, molecular shape, and hydrogen bonding. The large difference between the predicted and experimental densities of TATB is ascribed to extensive intramolecular and intermolecular hydrogen binding, which is also held responsible for the extraordinary stability and insensitivity of this material (Reference 4).
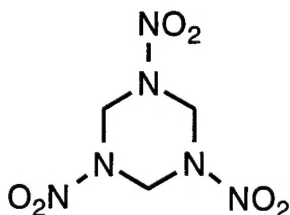
1 (RDX)

Density 1.80 (1.83) g/cm^3

VofD 8940 m/s

P_{CJ} 378 kbar

m.p. 204°C

$h_{50\%}$ 22-24 cm
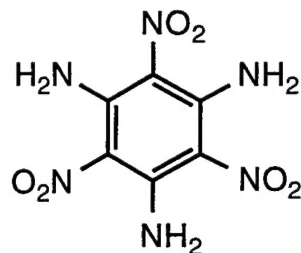
2 (TATB)

Density 1.78 (1.93) g/cm^3

VofD 7860 m/s

P_{CJ} 277 kbar

m.p. 350°C

10/10 NF @ 200 cm

We felt that high nitrogen compounds, substituted with nitro and amino groups and the *N*-oxide functionality where appropriate, may provide a source of these desired insensitive energetic materials. Classes of compounds investigated in this report include dibenzo-1,3a,4,6a-tetraazapentalenes, particularly those derived from 2,4,8,10-tetranitrodibenzo-1,3a,4,6a-tetraaza-pentalene (TACOT), and benzo-1,2,3,4-tetrazine-1,3-dioxides, with a little work related to polyaminopolynitropyridine-1-oxides also being described.

RESULTS AND DISCUSSION

DIBENZO-1,3a,4,6a-TETRAAZAPENTALENES

Interest and activity have continued in energetic materials derived from dibenzo-1,3a,4,6a-tetraazapentalene—i.e., TACOT chemistry. TACOT itself, (**3**), has high density, and outstanding thermal stability and explosive insensitivity, but its explosive performance is rather indifferent. The initial focus was on TATB-like variants, such as (**4**), which should have enhanced density and substantially improved performance, while the alternating amino and nitro groups should ensure the desired stability and insensitivity. It was intended that attention would then be turned towards more highly nitrated derivatives, which should show further enhancement of explosive performance, but would rely for their stability and insensitivity on the intrinsic stability of the dibenzo-1,3a,4,6a-tetraaza-pentalene skeleton.

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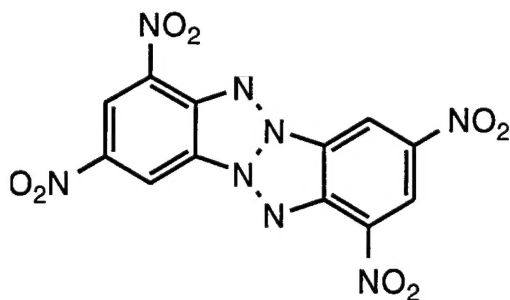
3 (TACOT)

Density 1.82 (1.83) g/cm³

VofD 7060 m/s

P_{CJ} 203 kbar

m.p. 410°C (dec)

10/10 NF @ 200 cm
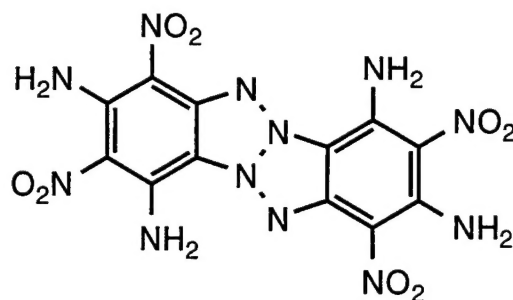
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Density 1.86 g/cm³

VofD 7570 m/s

P_{CJ} 250 kbar

Interest in this class of compounds as potential energetic materials was heightened by research initiated at the University of New Orleans (Reference 5). In particular, a compound was prepared from TACOT by a sequence of reactions involving nucleophilic displacement of two nitro groups by azide ion, nitration with 90% nitric acid, thermolysis, and finally a second nitration step using 100% nitric acid in trifluoromethanesulfonic acid. The sequence was fraught with uncertainties, beginning with some disagreement in the literature over the structure of TACOT itself, and compounded by the absence of absolute structural proof for any of the subsequent reaction products due to low solubilities and difficulties in obtaining crystals suitable for X-ray crystallography. The structure for the diazidodinitro compound (**5**) originally proposed by Carboni (Reference 6) was initially accepted at face value, and the succeeding steps seemed quite credible. The product proved to be surprisingly insensitive, assuming it to be the proposed structure; the impact sensitivity measured at the Naval Surface Warfare Center, White Oak Laboratory, Silver Spring, Md., was 148 centimeters (cm), compared with a value of 160 cm for 2,4,6-trinitrotoluene (TNT) (Reference 7). If it was indeed **8**, with empirical formula $C_{12}N_{12}O_{12}$, it should be extremely dense (2.00-2.06 grams/cubic centimeter (g/cm³)) (Reference 2), and with a detonation velocity of 8300 meter/second (m/s) and a detonation pressure of 319 kilobars (kbar) (Reference 3), it would be a valuable new dense, powerful but insensitive explosive ingredient.

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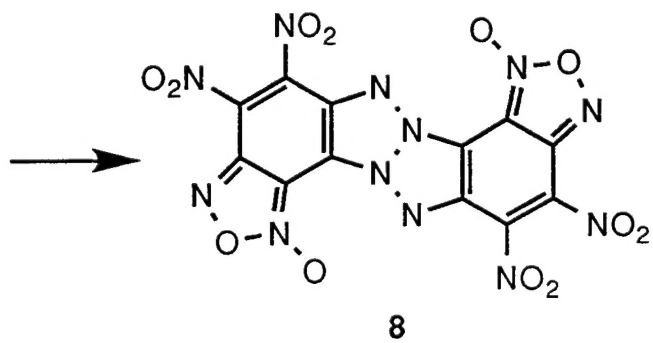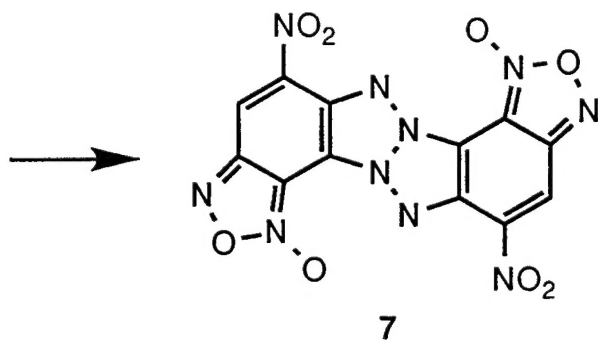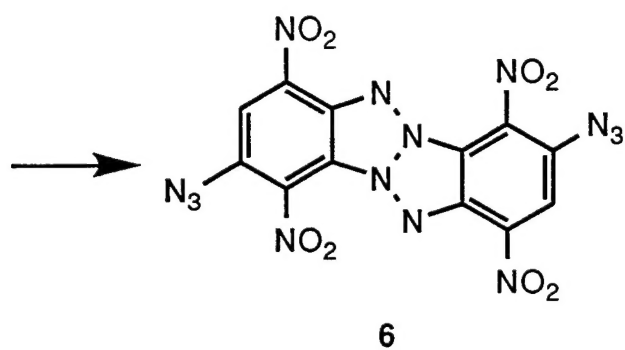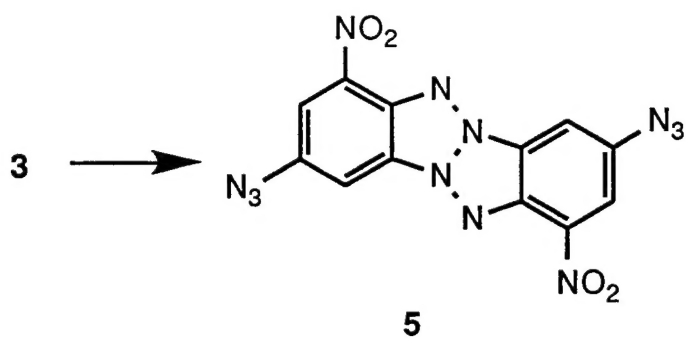
The reaction sequence was repeated in these laboratories, as well as at others including White Oak, the University of Southern California, Los Angeles, Calif., and Lawrence Livermore National Laboratory, Livermore, Calif., thereby confirming the essential mechanics of the process. However, the first progress in actually unraveling the structural puzzle was afforded by a single crystal X-ray structure of TACOT carried out at the Naval Research Laboratory (NRL), Washington, DC, and included in the Appendix. Figure A-1 confirmed the molecular structure **3** initially proposed (Reference 6), while Figure A-2 shows the herringbone assembly of molecules in the crystal.

The further reaction products proved to be even less soluble, making recrystallization to obtain material suitable for X-ray structure determination extremely difficult. This lack of solubility also made nuclear magnetic resonance (NMR) spectroscopy difficult; usually heating to 350 K was required, together with great care to ensure that the sample was fully dissolved. Furthermore, the diazido compounds produced in the first two reactions proved too unstable under these conditions to permit ^{13}C-NMR spectra to be obtained. The high melting points and low volatility of all products rendered mass spectroscopy difficult, and in many cases the parent ion could not be detected. Finally, elemental analysis of the ultimate product did not correspond satisfactorily with the proposed formula $C_{12}N_{12}O_{12}$. High nitrogen compounds are renowned for their poor elemental analyses, but on the other hand there was persistent evidence in both infrared and ^{1}H-NMR spectra for replaceable protons, presumably -OHs, which could not be removed by drying.

Ultimately, after exhaustive efforts, crystals were obtained at NRL suitable for X-ray analysis, and the hydrated structure **9** was determined (Reference 5). There was some initial uncertainty whether **9** was the structure of the material as prepared, or whether it was an impurity present in low concentration, or even an artifact produced during the crystallization process. However, subsequent investigations, and particularly NMR experiments (^{13}C solution state, and ^{13}C and ^{15}N solid-state cross-polarization/magic angle spinning (CP/MAS)) carried out at China Lake, led to the consensus that **9** is indeed the structure of the product, as prepared initially at the University of New Orleans and then repeated at White Oak, China Lake, and the University of Southern California. The elemental analyses correspond more satisfactorily with the structure **9**, while the poorer oxygen balance and lower nitrogen content of **9** make the low impact sensitivity more understandable.
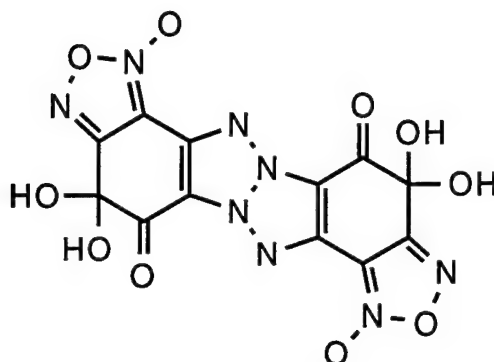
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As already noted, the limited solubility of the putative $C_{12}N_{12}O_{12}$ made spectroscopic analysis exceedingly difficult, and solid-state NMR was chosen as a starting point. The ^{13}C CP/MAS NMR spectrum of a sample prepared at White Oak is shown in Figure 1, with an expansion of the aromatic region shown in Figure 2. The spectrum contains thirteen major resonances, whose chemical shifts are indicated on the plots and in Table 1. Of these, the resonances at 2.0 and 116.1 ppm are due to acetonitrile, remaining from recrystallization. An "attached proton test" experiment indicated that the acetonitrile methyl group (2.0 ppm) contains the only protonated carbon in the sample.

TABLE 1. Correlation of ^{13}C-NMR Data for Putative $C_{12}N_{12}O_{12}$.[a]

White Oak Solid, ppm	White Oak DMSO, ppm	UNO[b] DMSO, ppm	USC DMSO, ppm	China Lake DMSO, ppm
2.0[c]	1.1[c]	...	...	...
90.2	89.5	...	89.5	...
107.0	**104.1**	**103.1**	**104.1**	**104.0**
111.9	**114.9**	**113.9**	**114.8**	**114.9**
116.1[c]	118.1[c]	...	...	118.0[c]
121.5	124.2	...	...	...
140.8	**138.5**	**137.5**	**138.4**	**138.5**
145.2	...	...	...	...
148.3	**150.3**	**149.4**	**150.4**	**150.3**
156.4	157.5	...	...	...
165.4	**164.5**	**163.5**	**164.5**	**164.5**
170.2	**167.7**	**166.6**	**167.6**	**167.6**
179.3	...	...	178.6	...

[a] Items that are in bold type emphasize correspondence of peaks in different samples.
[b] University of New Orleans
[c] Acetonitrile
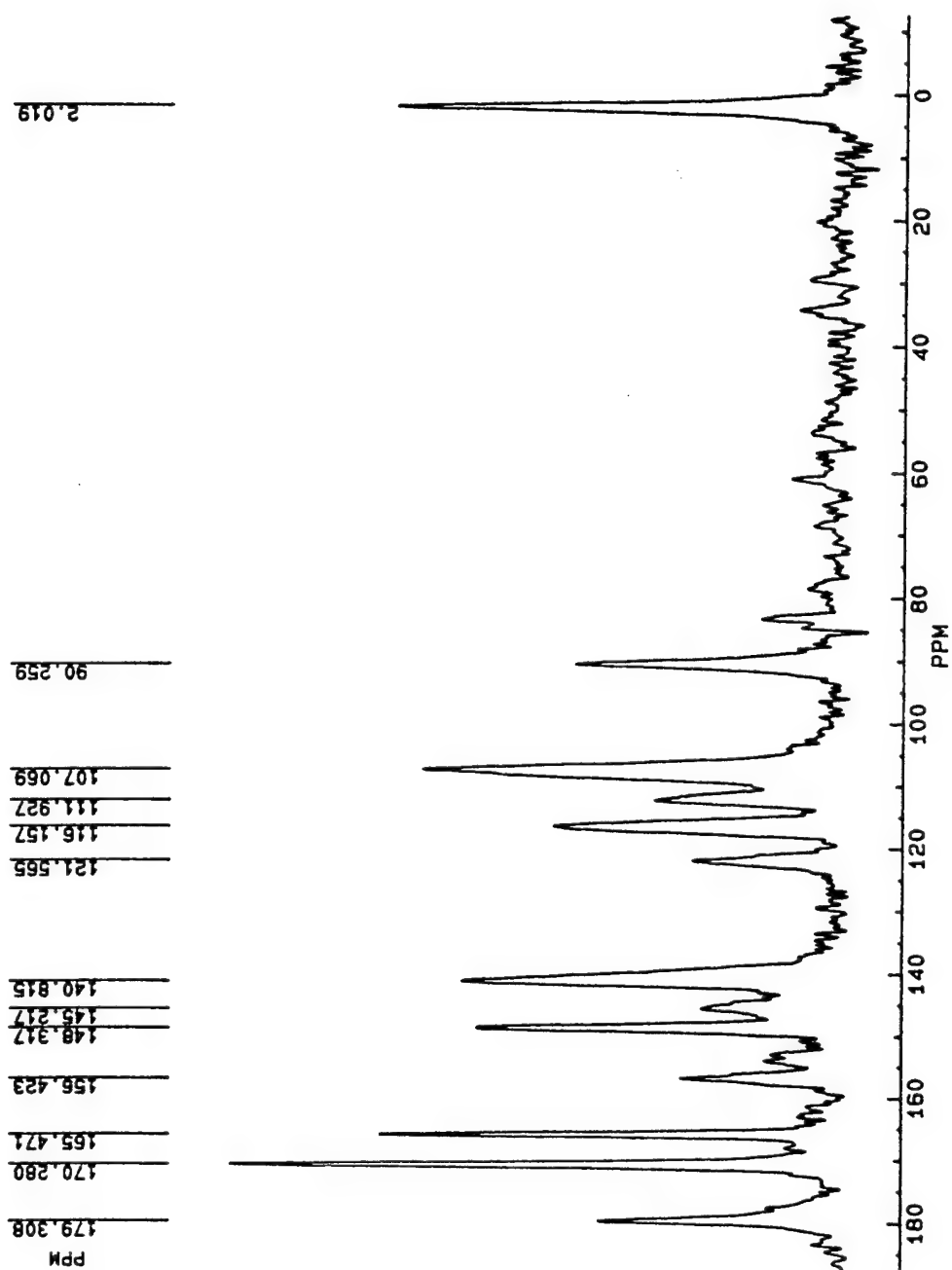
FIGURE 1. ^{13}C CP/MAS NMR Spectrum of Compound **9**, Prepared at White Oak.
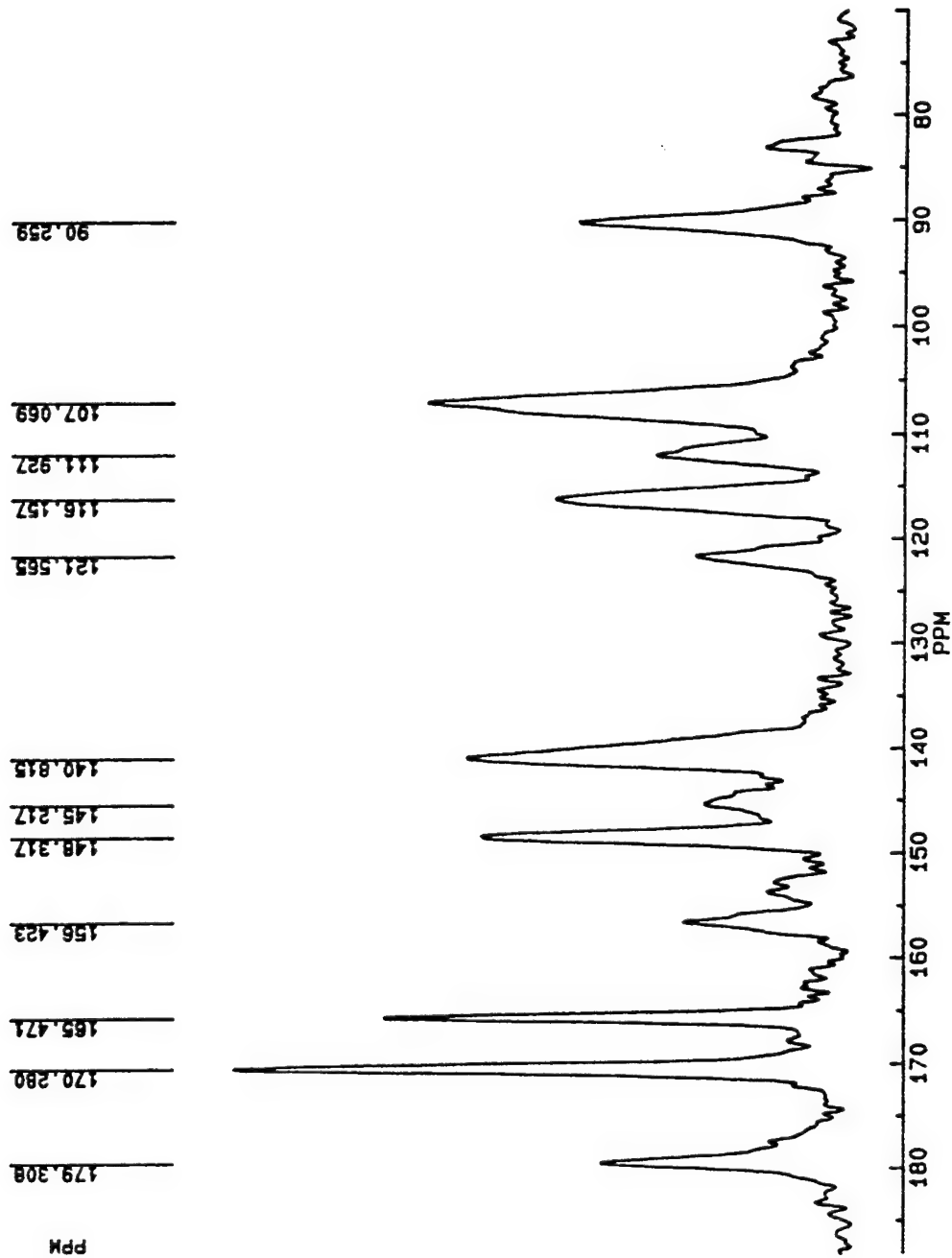
FIGURE 2. 13C CP/MAS NMR Spectrum of Compound **9**, Prepared at White Oak—Expansion of the Aromatic Region.

A solution ^{13}C NMR spectrum of this White Oak sample was then run in d_6-dimethylsulfoxide (DMSO) at 350 K. It became apparent that the product is somewhat unstable under these conditions, as illustrated by Figure 3, showing the ^{13}C NMR spectrum of a freshly prepared solution and that of a solution held at ambient temperature for 96 hours (h). Chemical shifts for this freshly prepared solution are presented in Table 1, as are the spectra of samples prepared and recorded at the University of New Orleans, the University of Southern California, and China Lake (also reproduced in Figure 4).

Initially, the apparent inconsistencies between the spectra and presence of more than the six resonances expected for a symmetrical product seemed puzzling, but these observations can be rationally accounted for. First, the presence of acetonitrile (1.1-2.0 and 116.1-118.0 ppm) has already been noted. Second, the differences in chemical shifts in the solid and solution spectra of the White Oak sample can be accounted for in terms of solvent and crystal field effects. Small changes in chemical shift frequently arise from crystal orientation effects in the solid, from solvent effects in solution, and from differences in bulk magnetic susceptibility. Third, the presence of additional resonances in the solid-state spectrum of the White Oak sample (145.2. 156.4(?), 179.3 ppm) could arise from solvation effects (^{13}C relaxation time T_1 does not play a significant role in solid-state CP/MAS NMR or from impurities insoluble in DMSO). Finally, there is marked consistency of the chemical shifts of the six major resonances of samples prepared at White Oak, the University of Southern California, and China Lake, while those measured at the University of New Orleans are consistently 0.9-1.0 ppm lower; this minor discrepancy may be attributed to differences in referencing. It is, therefore, clear that the same material was indeed prepared in each establishment.

The conclusion that the structure of the final product was **9** rather than the desired $C_{12}N_{12}O_{12}$ (**8**) or its isomer was based on the following observations.

1. The ^{13}C chemical shifts listed in Table 1 are not consistent with those expected for the $C_{12}N_{12}O_{12}$ isomers. Based on the ^{13}C NMR spectrum of dibenzotetraazapentalene itself (Reference 8), combined with the increments calculated for the furoxan ring (Reference 9) and the aromatic additivity rules (Reference 10), the ^{13}C chemical shifts fo **8** were estimated to be 104, 107, 131, 135, 141, and 141 ppm, while those of the alternative isomer are 109, 112, 125, 130, 137, and 151 ppm. While only estimates, these values are expected to be reasonable guides. However, there are considerable discrepancies with the experimental results, and particularly the resonances at 164.5 and 167.6 ppm, which correspond better with carbons bonded to oxygen.

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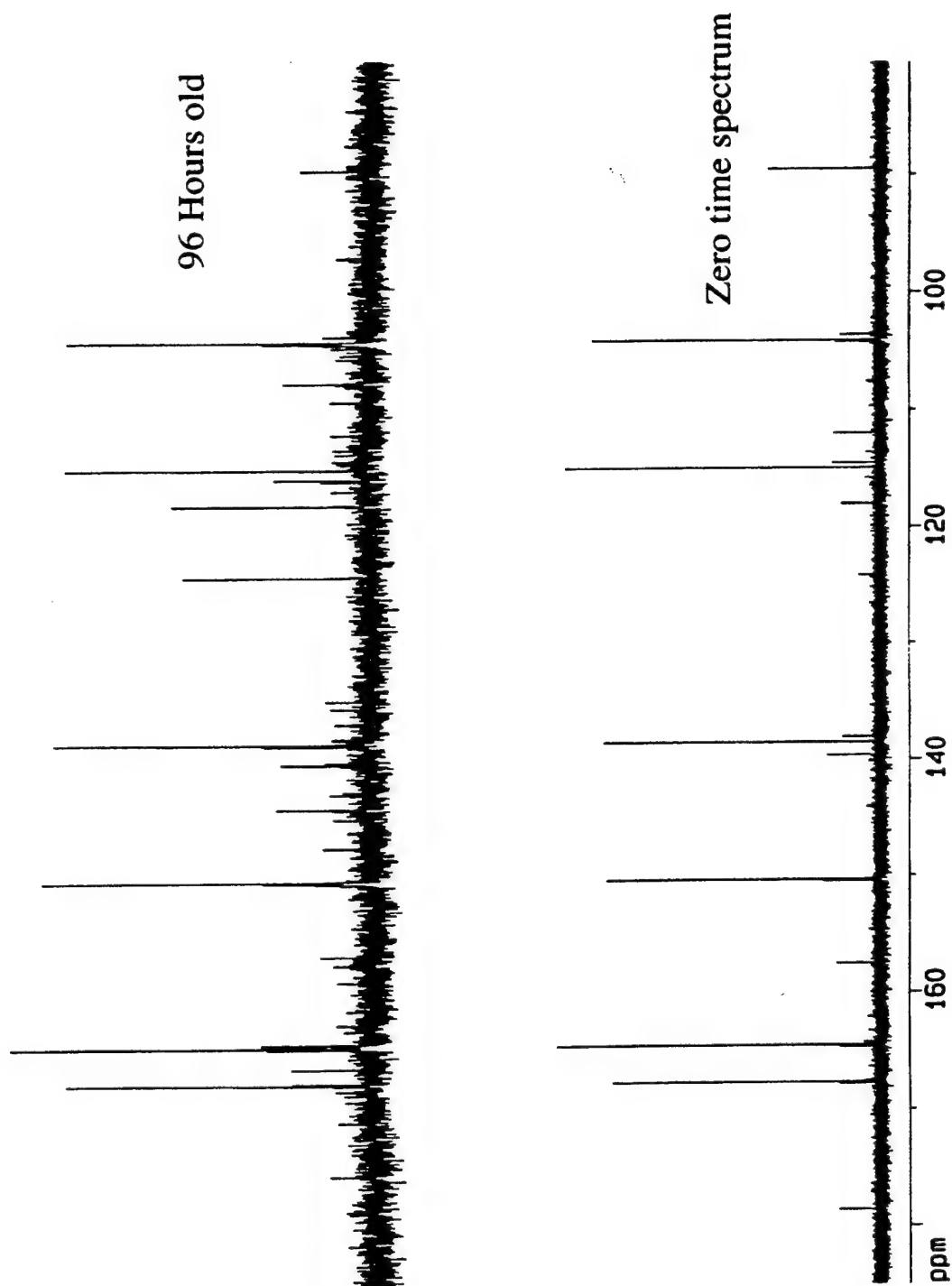
FIGURE 3. Solution ^{13}C NMR Spectrum of Compound **9** (prepared at White Oak), Run in DMSO at 350 K. (Bottom) Freshly made solution; (top) after 96 h at ambient temperature.

FIGURE 4. Solution 13C NMR Spectrum of Compound 9 (prepared at China Lake), Run in DMSO at 350 K.
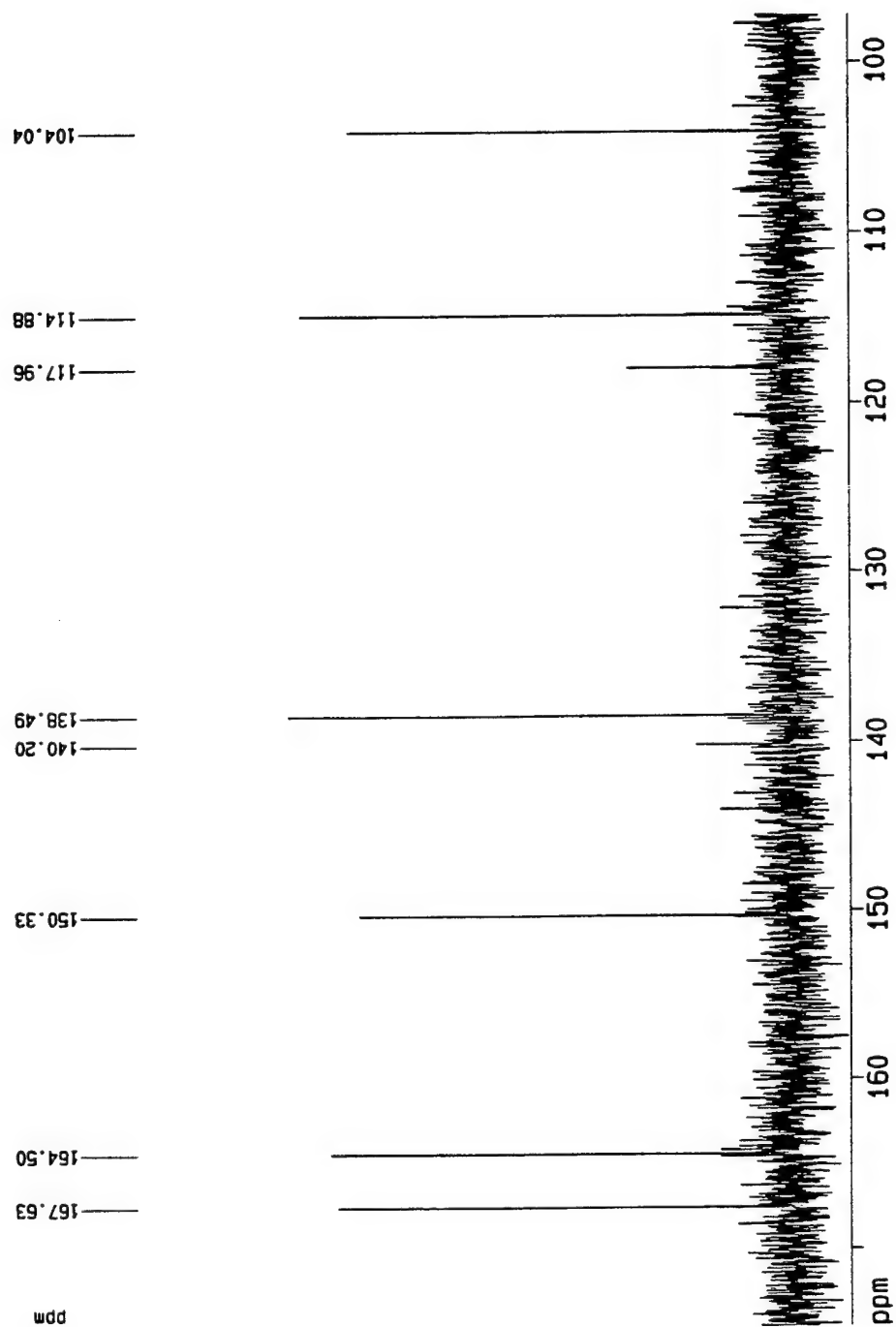
2. Inspection of the solid-state spectrum in Figures 1 and 2 shows that the resonances at 165.4 and 170.2 ppm are markedly sharper than the other resonances. This is typical of solid-state ^{13}C resonances of carbons bonded to oxygen rather than nitrogen; resonances for carbons bonded to nitrogen tend to be broadened in solid-state CP/MAS spectra.

3. A ^{15}N CP/MAS NMR spectrum was recorded on the White Oak sample (a 7-day run was required), and is given in Figure 5. The spectrum shows four clear resonances at 30.7, -14.8, -108.5, and -140.4 ppm, with a sharp dispersive feature at ca. -25 ppm identified as an artifact. The resonances at 30.7 and -14.8 ppm are assigned to the furoxan ring, while those at -108.5 and -140.4 ppm are assigned to the tetraazapentalene nitrogens. The number and chemical shifts of these resonances are consistent with structure **9**, while six resonances would be expected for **8** or its isomers, with the nitro group nitrogens around 0 ppm.

The original procedure (Reference 5) called for nitration using 100% nitric acid in trifluoromethanesulfonic acid, with workup by quenching in ice water; it was suspected that **9** was formed from **8** by rearrangement/hydrolysis/oxidation during this aqueous workup procedure. However, we have found that the reaction can be carried out using 100% nitric acid in the presence of Nafion NR50 beads, and evaporation of the nitric acid under reduced pressure to avoid the aqueous workup afforded the same product **9**, which was isolated even when dinitrogen pentoxide was present in the nitration mixture to scavenge any water generated during the reaction. It, therefore, appears that **9** is not formed by hydrolysis of the tetranitro derivative either in the nitration medium or during workup.

In an attempt to remove the replaceable protons (presumed at the time to be water of crystallization) from the putative compound (**8**), researchers at White Oak heated the material to about 110°C, whereupon, they observed a simplification of the infrared spectrum and virtual disappearance of the -OH feature, and they isolated a compound to which they ascribed the quinonoid structure **10** (Reference 5). We found that the same transformation of **9** into **10** could occasionally be brought about simply by recrystallization from dry acetonitrile.
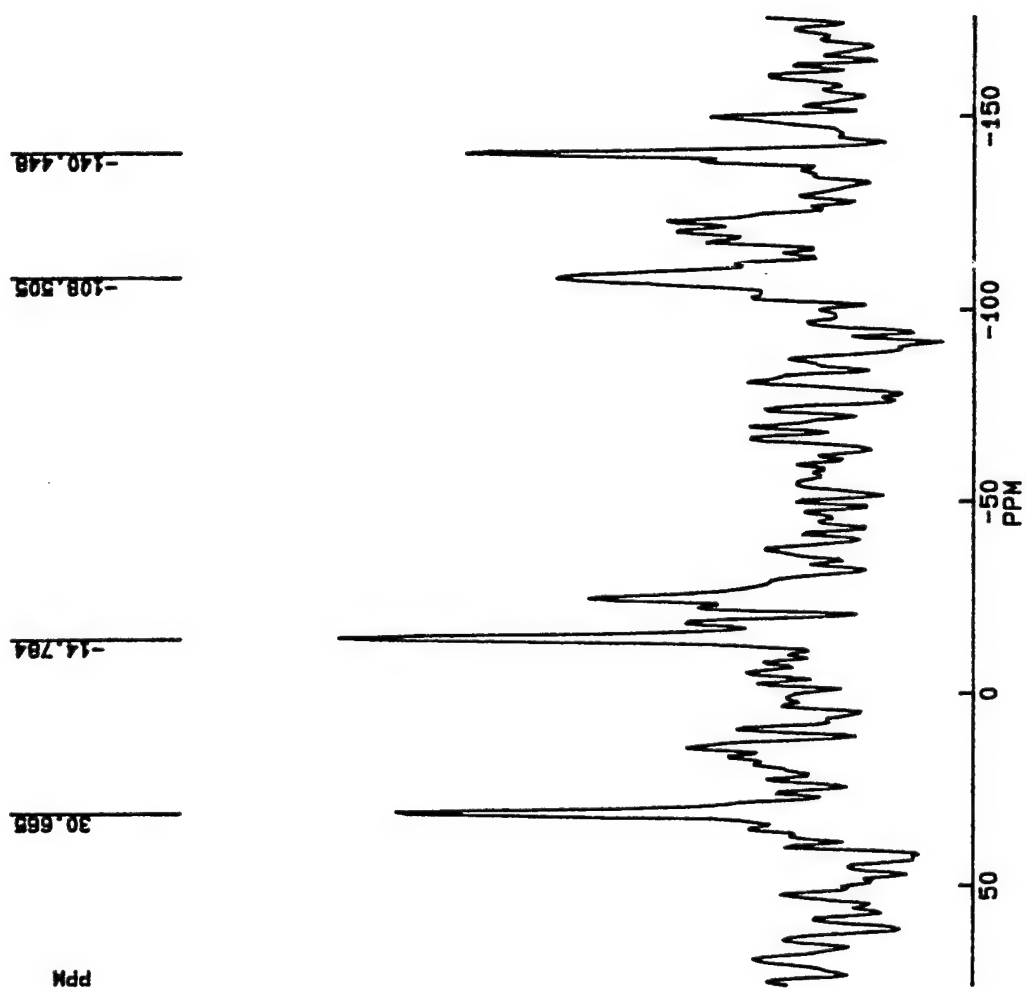
FIGURE 5. 15N CP/MAS NMR Spectrum of Compound **9**, Prepared at White Oak.
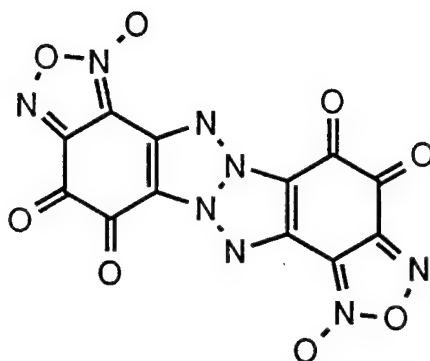
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The formation of **9** could conceivably be rationalized from **8**, but would necessitate a convoluted series of rearrangements (or at least equilibria) of the furoxan ring systems, followed by nitro-nitrito rearrangement, hydrolysis, and oxidation. These furoxan rearrangements are well known in the benzofuroxan series, and are illustrated in Schemes 1 and 2. Scheme 1 involves opening of the furoxan ring and the reclosure, with an effective migration of the exocyclic oxygen (Reference 11); Scheme 2 involves interaction of the furoxan with an adjacent nitro group, with an effective migration of the furoxan moiety around the benzene ring—the so-called Boulton-Katritzky rearrangement (Reference 12).

Scheme 1
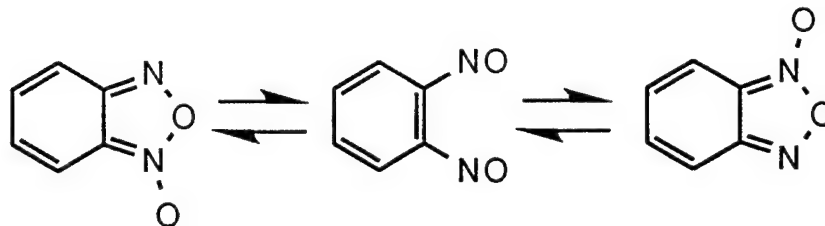
Scheme 2
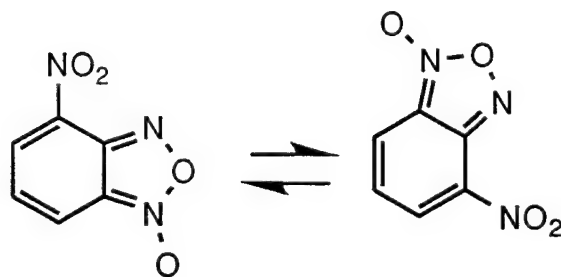
As noted above, the structure initially assigned by Carboni for the diazido-dinitro derivative was the 2,8-diazido-4,10 dinitro-isomer (**5**) (Reference 6). Mitigating against this structure was the ^{1}H-NMR spectrum, which showed two doublets (J = 1.92 Hz) at 9.03 and 8.15 ppm. These signals are more consistent with the alternative 4,10-diazido-2,8-dinitro isomer (**11**). (Analysis of this spectrum was made difficult by the low solubility of the material, which necessitated the spectrum being recorded at 350 K, by the presence initially of a monoazidotrinitro intermediate (5 to 10%, essentially eliminated in later experiments), and by an unexpected transformation of the product in DMSO under these conditions. This transformation is not well characterized, but probably involves the formation of some sort of complex in solution. Formation of solvent complexes of TACOT has been described (Reference 13). Note that the diazidodinitro compound was indeed prepared in and isolated from DMSO, and the transformation must, therefore, be reversible. However, its existence did preclude recording a ^{13}C-NMR spectrum.) Treatment of the diazidodinitro compound with triphenylphosphine in benzene or ethanol, either at ambient temperature or under reflux, gave a highly insoluble, intensely purple solid, presumed to be the phosphinimine derivative. Hydrolysis using concentrated hydrochloric acid in glacial acetic acid under reflux gave the corresponding acetamide. Recrystallization from DMSO gave crystals that were solvated but suitable for single crystal X-ray structure determination; analysis at the NRL Laboratory for the Structure of Matter (Figure A-4) revealed that the hydrolysis product was indeed 4,10-bis(acetamido)-4,10-dinitrodibenzo-1,3a,4,6a-tetraazapentalene (**13**). Given the mild reaction conditions used and the high yields obtained, it may then be concluded that the phosphinimine was **12**, and that the diazidodinitro compound was, therefore, 4,10-diazido-2,8-dinitrodibenzo-1,3a,4,6a-tetraazapentalene (**11**) rather than the alternative isomer (**5**) originally proposed by Carboni (Reference 6).

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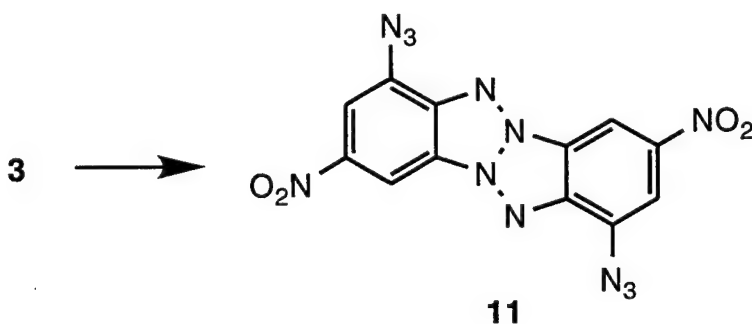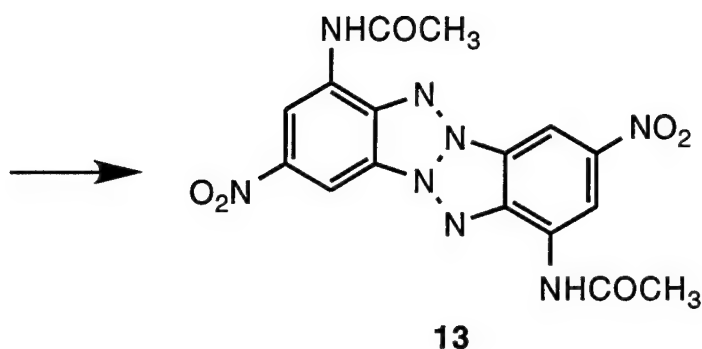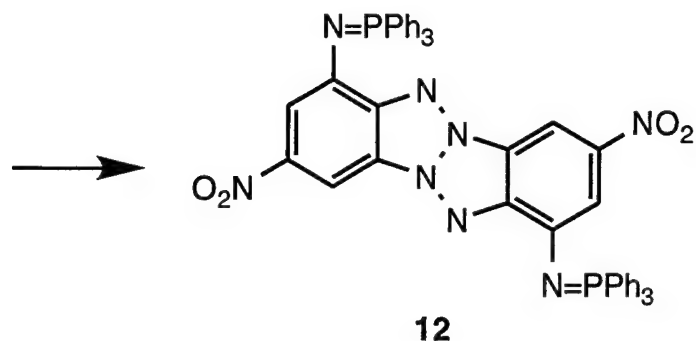
Nitration of **11** would give 4,10-diazido-2,3,8,9-tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (**14**) rather than the isomer (**6**), and thermolysis of **14** would yield the bisfuroxan **15**. Indeed, single crystal X-ray diffraction studies at the University of New Orleans (Reference 5) have confirmed this structure, a result corroborated independently at the University of Southern California. The generation of **9** on further nitration may then be readily rationalized either by direct oxidation of **15**, or through the intermediacy of the tetranitrobisfuroxan (**16**). The latter compound might well be hydrolytically unstable, but our inability to isolate it even in anhydrous reaction conditions and without aqueous workup suggests the direct oxidation route.

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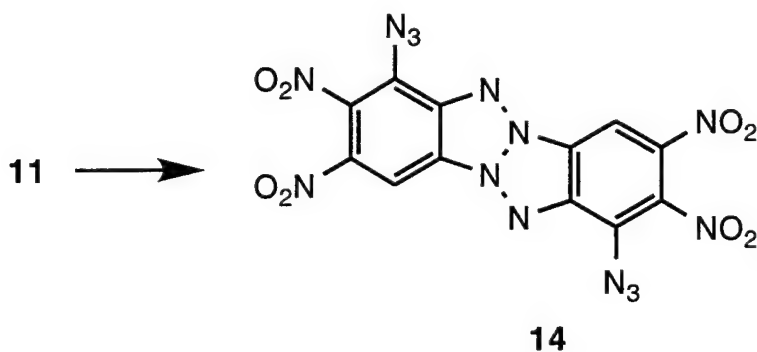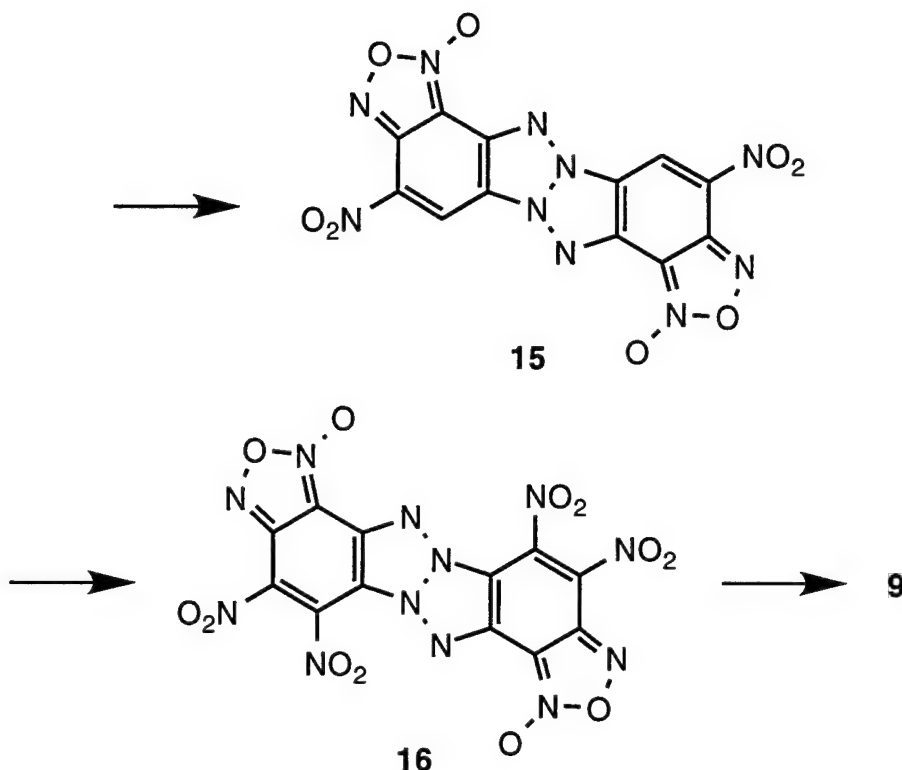
BENZO-1,2,3,4-TETRAZINE-1,3-DIOXIDES

Tartakovskii first reported the synthesis of benzo-1,2,3,4-tetrazine-1,3-dioxides in 1990 (Reference 14). Among the compounds described were the parent heterocycle (**17**), whose structure was confirmed by single crystal X-ray crystallography (Reference 15), and several nitro derivatives, including 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (**18**). The latter compound appears to be quite stable, with a reported melting point of 209-211°C, and our predictive calculations estimate for it a density of 1.85 g/cm^3 (Reference 2), a detonation velocity of 8230 m/s and a detonation pressure of 312 kbar (Reference 3). It was logical to suggest, by analogy with TATB and 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) (Reference 16), that the amino derivative 6,8-diamino-5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (**19**) might also be an insensitive explosive, for which a density of 1.87 g/cm^3 (Reference 2), a detonation velocity of 8490 m/s, and a detonation pressure of 336 kbar (Reference 3) may be predicted.

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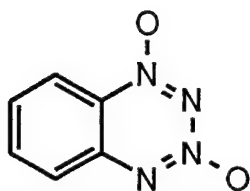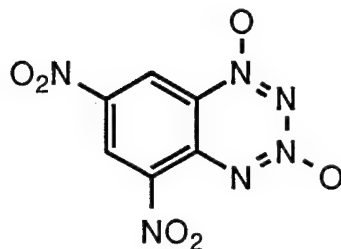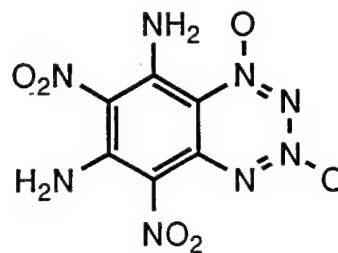
Density 1.85 g/cm^3

VofD 8230 m/s

P$_{CJ}$ 312 kbar

m.p. 209-211°C

19

Density 1.87 g/cm^3

VofD 8490 m/s

P$_{CJ}$ 336 kbar

The literature method for the synthesis of **17** and **18** is sketchy, but accurate. Indeed, the poorest yield was for the initial step, oxidation of *o*-nitroaniline to *o*-nitrosonitrobenzene using potassium persulfate in dilute sulfuric acid, achieved in only about 40% yield (Reference 17). Condensation with *N,N*-dibromo-*tert*-butylamine gave 2-*tert*-butyl-1-(2-nitrophenyl)-diazene-1-oxide (**20**) in 94% yield (Reference 18), while reduction with stannous chloride in a mixture of ethanol and ethyl acetate afforded 2-*tert*-butyl-1-(2-anilino)-diazene-1-oxide (**21**) in 76% yield (Reference 14), together with a trace of 2-azoxyaniline. Tartakovskii reports that **21** may be converted to a mixture of **17** and its 5-nitro, 7-nitro and 5,7-dinitro derivatives by oxidation with dinitrogen pentoxide in an organic solvent (Reference 14). We obtained **18** in 79% yield by oxidation of **21** with dinitrogen pentoxide in dichloromethane at -20°C, and immediately nitrating the product mixture with 100% nitric acid in 20% oleum and raising the temperature to 80°C, under which conditions the excess nitrogen pentoxide and dichloromethane boiled off.

20

21

17   **18**
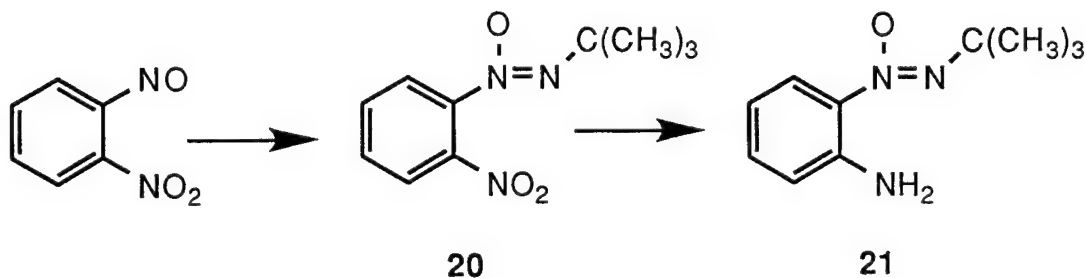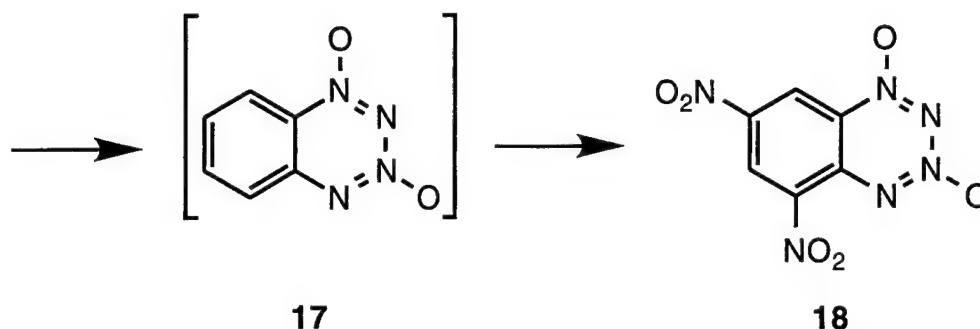
Recrystallization of 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (**18**) from 1,2-dichloroethane gave crystals suitable for single crystal X-ray structure determination at the Laboratory for the Structure of Matter, NRL. These studies confirmed the expected structure, and revealed a crystal density of 1.832 g/cm^3. Compound **18** packs with two distinct molecules in the asymmetric unit, molecules which differ primarily in their packing contacts. Both molecules are semiplanar (Figure A-6), the only deviations being a slight out-of-plane twist for the nitro group closest to the ring junction in each case, 22° at N(5) in the molecule **18A** and 24° at N(15) in the molecule **18B**. The two molecules, **18A** and **18B**, that comprise the asymmetric unit do not intermingle in the crystal. Molecule **18A** (labeled N(1) to C(8A)) and its symmetry mates form a double layer that meanders about the y = 1/2 plane, in a manner that can be described as a "double pleated sheet" (Figure A-7). Molecule **18B** (whose atoms are labeled N(11) to C(18A)) packs in a double layer that straddles the y = 0 plane, but in this case the double layer is of the herringbone type (Figure A-8). Since the simplest view of "layer **A**" is along Z, and that of "layer **B**" is along X, no single view of the cell can be used to illustrate the packing superstructure simply. The closest packing approaches differ in the two types of layers. The closest intermolecular distance, 2.80 Å, is in the N-oxide atom O(3) to a nitro nitrogen atom N(5) of a two-fold screw-related molecule in the "layer **A**." There are no such close N...O approaches in the "layer **B**." Both layers contain several nitro oxygen to benzene carbon approaches in the short 2.9-3.1 Å range. Finally, **18** had a drop-weight (2.5 kilogram (kg)) impact sensitivity of 15 cm, making it comparable in sensitivity with pentaerythritol tetranitrate (PETN).

PYRIDINE-1-OXIDES

An earlier report detailed synthetic approaches towards 3,5-diamino-2,4,6-trinitropyridine-1-oxide (**22**), for which high density and good performance were predicted (Reference 8). If this compound has the extensive hydrogen bonding expected, it should be a desirable powerful insensitive explosive.

21

22

Density 1.90 g/cm^3

VofD 8650 m/s

P_{CJ} 351 kbar

3,5-Dimethoxy-2,6-dinitropyridine (**24**) was prepared by mixed acid nitration (70% nitric acid in 98% sulfuric acid) of 3,5-dimethoxypyridine (**23**) at 40°C (Reference 19), and was converted to 3,5-diamino-2,6-dinitropyridine (**25**) by treatment with ethanolic ammonia. (Crystals suitable for X-ray analysis were not obtained, but the ^{1}H-NMR spectrum in DMSO showed one broad signal for the amine protons, indicating free rotation about the C-N bond, and hence the absence of hydrogen bonding.)

23   **24**   **25**
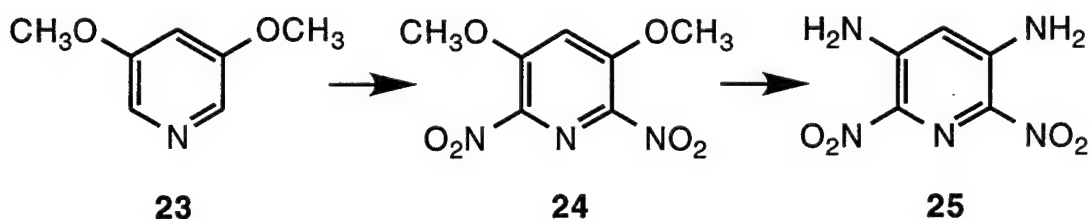
3,5-Dimethoxy-2,6-dinitropyridine-1-oxide (**27**) was prepared by mixed acid nitration (70% nitric acid in 98% sulfuric acid) of 3,5-dimethoxypyridine-1-oxide (**26**) (Reference 19), this time at 90°C. However, rather than displacing the methoxyl groups to yield the desired 3,5-diamino-2,6-dinitropyridine-1-oxide (**28**), reaction in ethanolic ammonia resulted instead in displacement of the 2-nitro group (clearly activated towards nucleophilic attack by the adjacent *N*-oxide functionality) to give the unexpected 2-amino-3,5-dimethoxy-6-nitropyridine-1-oxide (**29**).

26 → **27** → **28**

27 → **29**
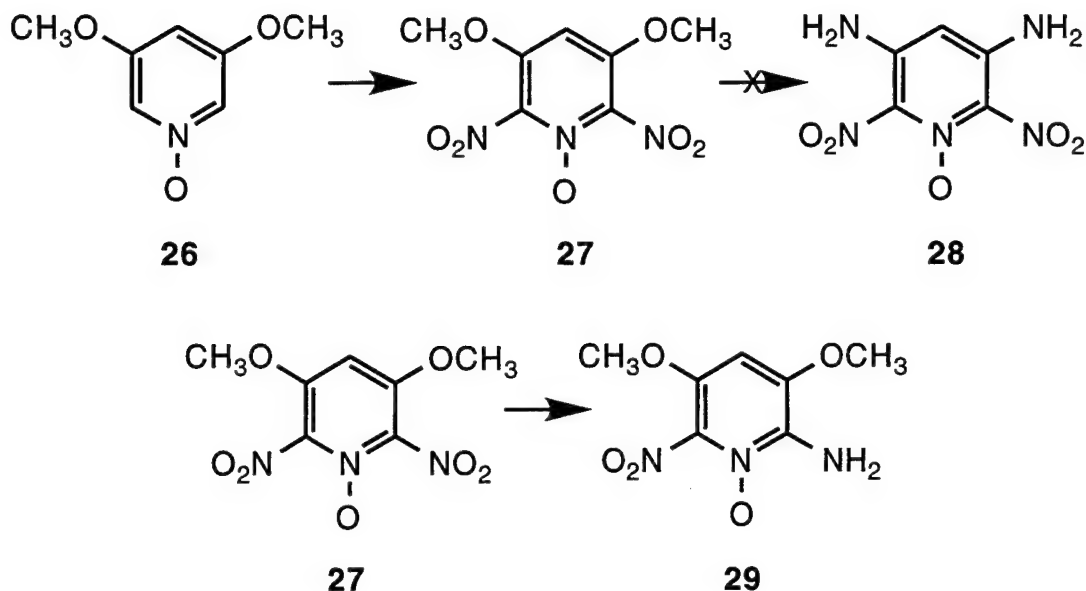
2,6-Diamino-3,5-dinitropyridine (**30**, R=H) was converted smoothly and in high yield to 2,6-diamino-3,5-dinitropyridine-1-oxide (**31**, R=H) by heating with 30% hydrogen peroxide in glacial acetic acid under reflux (Reference 20). 2,4,6-Triamino-3,5-dinitropyridine (**30**, R=NH$_2$) was also oxidized to the *N*-oxide (**31**, R=NH$_2$), although the yield was low due to solubility limitations (Reference 21). However, 3,5-diamino-2,6-dinitropyridine (**25**) was unaffected by these conditions, and was recovered unchanged without a trace of **28**. The isomer **25** was also unaffected by oxidation by 30% hydrogen peroxide in trifluoroacetic acid at ambient temperature, but suffered gross decomposition when the reaction was carried out under reflux conditions. Alternative oxidizing systems, such as magnesium monoperoxyphthalate hexahydrate in dichloroethane (Reference 22), urea hydroperoxide in trifluoroacetic acid (Reference 22), and even *m*-chloro-perbenzoic acid and hydrofluoric acid in DMF and methanol (Reference 23), were equally ineffectual.

30 → **31**

R = H, NH$_2$

23

25 → **28**

Attempts at further nitration of 2,6-dinitropyridines and the N-oxide derivatives were also unsuccessful. Prolonged nitration of 3,5-dimethoxy-2,6-dinitropyridine (**24**) and its N-oxide (**27**) using mixed acid (100% nitric acid in 98% sulfuric acid) at elevated temperatures (up to 90°C) gave only water-soluble degradation products. Nitration of diamino aromatics is seldom successful, usually giving only decomposition by ring scission; such also proved to be the case on attempted nitration of 3,5-diamino-2,6-dinitropyridine (**25**). An alternative approach was examined, involving nitration of 3-amino-5-methoxy-2,6-dinitro-pyridine (**32**). However, mixed acid nitration conditions or nitration in acetic acid, with or without the presence of acetic anhydride (conditions which favor formation of nitramines), resulted only in generation of brown oxides of nitrogen and water-soluble degradation products.

32

CONCLUSIONS AND RECOMMENDATIONS

Synthesis of the purported $C_{12}N_{12}O_{12}$, first derived from TACOT (2,4,8,10-tetranitrodibenzo-1,3a,4,6a-tetraazapentalene) at the University of New Orleans, has been repeated. Nuclear magnetic resonance experiments (^{13}C solution-state, and ^{13}C and ^{15}N solid-state CP/MAS), in concert with research at other establishments, has identified the structure of this material. Single crystal X-ray diffraction experiments have correctly identified the structure of a key intermediate in the synthetic sequence, thereby identifying the reaction pathway. Future research will be devoted to the chemistry of the related benzo-1,3a,4,6a-tetraazapentalenes.

The synthetic route to 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide has been successfully repeated, and the structure has been confirmed by single crystal X-ray diffraction experiments. This material has sensitivity comparable with PETN, with a drop-weight impact sensitivity of 15 cm. Future work will be directed towards amination of this product.

Attempts at further nitration and oxidation of 3,5-diamino-2,6-dinitro-pyridine to afford 3,5-diamino-2,4,6-trinitropyridine-1-oxide have not been successful. Future efforts at the synthesis will be by an alternative approach involving amination of the known 2,4,6-trinitropyridine and its N-oxide.

EXPERIMENTAL SECTION

WARNING: Many of the compounds described in this report are potential explosives, which may be subject to accidental initiation by such environmental stimuli as impact, friction, heat, or electrostatic discharge. Therefore, appropriate precautions should be taken in their handling and/or use. Melting points were determined in capillary tubes using a Mel-Temp II melting point apparatus, or a DuPont Instruments DSC 2910 differential scanning calorimeter. Infrared (IR) spectra were determined in KBr disks using a Perkin-Elmer Model 1330 spectrophotometer or as diffuse reflectance spectra run on a Nicolet 60SX FT-IR spectrophotometer. ^{1}H-NMR spectra were determined in d_6-acetone or DMSO solutions, using a Bruker AMX-400 instrument at 400 MHz; ^{13}C-NMR spectra were recorded on the latter instrument at 100 MHz. The various two-dimensional NMR experiments were also carried out on this instrument. Solid-state CP/MAS NMR spectra were obtained on a Bruker MSL-200 spectrometer (200 MHz), operating with a 90° pulse length of 5 micro-seconds (μs) and MAS rates of 3 to 4 kilohertz (kHz). ^{1}H and ^{13}C spectra are referenced to external TMS. ^{15}N spectra are referenced to external ammonium nitrate (nitrate at 0.0 ppm). Mass spectra were determined using a Perkin-Elmer 5985 gas chromatograph/mass spectrometer (GC/MS).

4,10-DIAZIDO-2,8-DINITRODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (4,10-DIAZIDO-2,8-DINITRO-5,11-DEHYDRO-5H,11H-BENZOTRIAZOLO-[2,1-a]BENZOTRIAZOLE) (11)

2,4,8,10-Tetranitro-1,3a,4,6a-tetraazapentalene (TACOT, **3**) (3.10 g, 8.0 millimoles (mmol)) was added to DMSO (65 milliliter (mL)) and heated to 100°C. Sodium azide (1.95 g, 30.0 mmol) was added slowly and with stirring, and the mixture was heated at 100°C for 1 h, turning very deep red in color. The mixture was allowed to cool to ambient temperature overnight, and the orange solid was

filtered off and washed with ethanol (10 mL) and finally ether (10 mL) to give **11** (1.33 g, 46%), m.p. 197°C (dec) (lit. 200°C (dec) (Reference 6)). IR: 2120, 1600, 1525, 1360, 1330, 1290, 1135, 960, 880, 810, 740 cm^{-1}. ^{1}H-NMR (DMSO, 350°C, recorded quickly): 9.03 (d, J = 1.92 Hz, H$_{1,7}$), 8.15 (d, J = 1.92 Hz, H$_{3,9}$).

4,10-BIS(TRIPHENYLPHOSPHINIMINO)-2,8-DINITRODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (4,10-BIS(TRIPHENYLPHOS-PHINIMINO)-2,8-DINITRO-5,11-DEHYDRO-5*H*,11*H*-BENZOTRI-AZOLO[2,1-*a*]BENZOTRIAZOLE) (12)

Triphenylphosphine (0.80 g, 3.05 mmol) was dissolved in benzene (200 mL) at ambient temperature, and 4,10-diazido-2,8-dinitrodibenzo-1,3a,4,6a-tetraazapentalene (**11**) (0.50 g, 1.30 mmol) was added. The reaction mixture was stirred for 48 h, to give a purple solution and a dark purple solid. Filtration gave a purple solid (1.00 g, 90%), m.p. 377°C (dec). The same product was obtained when the reaction was carried out in ethanol at ambient temperature for 24 h or in benzene solution under reflux for 4 h. This material was too insoluble for measurement of NMR spectra, but the IR spectra displayed clean, sharp signals, with a notable absence of any azide signals around 2100 cm^{-1}. The compound was tentatively identified with the structure **12**. IR: 1600, 1515, 1495, 1440, 1355, 1335, 1370, 1110, 1090, 730, 700, 530 cm^{-1}. M/z: 848 (parent ion, discernible), 278, 78 (base peak).

4,10-BIS(ACETAMIDO)-2,8-DINITRODIBENZO-1,3a,4,6a-TETRAAZA-PENTALENE (4,10-BIS(ACETAMIDO)-2,8-DINITRO-5,11-DEHYDRO-5*H*,11*H*-BENZOTRIAZOLO[2,1-*a*]BENZOTRIAZOLE) (13)

4,10-Bis(triphenylphosphinimino)-2,8-dinitrodibenzo-1,3a,4,6a-tetraaza-pentalene (**12**) (0.58 g, 0.68 mmol) was added to glacial acetic acid (50 mL), followed by concentrated hydrochloric acid (5 mL), and the mixture was heated under reflux with stirring over the weekend, during which time a brick-red solid was formed. The solid was filtered off and washed by heating overnight in ethanol (50 mL) under reflux. Filtration and drying gave 0.23 g (82%); recrystallization from DMSO gave 4,10-bis(acetamido)-2,8-dinitrodibenzo-1,3a,4,6a-tetraazapentalene (**13**) (solvated with one mole of DMSO) (0.22 g, 67%), m.p. 408°C (dec) (endotherm at ca. 130°C; loss of DMSO). IR: 3260, 3200, 3140, 3100, 3040, 1670, 1605, 1540, 1370, 1350, 1320, 1280, 1260, 1220, 1180, 1090, 1050, 1010, 950, 890, 860, 810, 740, 730, 700 cm^{-1}. ^{1}H-NMR (DMSO): 10.63 (br s, 2 H, NH's), 9.22 (d, J = 2.06 Hz, H$_{1,7}$), 8.74 (d, J = 2.06 Hz, H$_{3,9}$), 2.53 (s, 6 H, (CH$_3$)$_2$SO), 2.33 (s, 6 H, COCH$_3$'s). ^{13}C-NMR (DMSO): 169.64 (CO's), 142.50 (C$_{2,8}$), 140.72 (C$_{1a,7a}$), 128.06 (C$_{4,10}$), 117.25 (C$_{4a,10a}$), 110.35 (C$_{1,7}$), 102.96 (C$_{3,9}$), 39.71 ((CH$_3$)$_2$SO), 23.51 (CH$_3$'s). (Assignments are

not unequivocal.) M/z: 412 (parent ion), 370, 328 (base peak), 282, 78, 63. DMSO was also separated and detected (78 (parent ion), 63 (base peak)).

2,8-DINITRO-3,4,9,10-BISFUROXANODIBENZO-1,3a,4,6a-TETRAAZA- PENTALENE (2,8-DINITRO-3,4,9,10-BISFUROXANO-5,11-DEHYDRO- 5*H*,11*H*-BENZOTRIAZOLO[2,1-*a*]BENZOTRIAZOLE) (15)

Ninety percent nitric acid (20 mL) was cooled in an ice bath, and 4,10-diazido-2,8-dinitrodibenzo-1,3a,4,6a-tetraazapentalene (11) (5.33 g, 1.40 mmol) was added in portions. The reaction mixture was stirred at 0°C for 3 to 4 h, and was then quenched in ice water (400 mL). Filtration, washing with water, and drying at the pump gave an orange-brown solid (4.2 g, 64%), identified from its ^{1}H-NMR spectrum (DMSO) (9.50, s) as 4,10-diazido-2,3,8,9-tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (14), containing about 5% of impurity. This diazido compound also proved unstable in DMSO over any prolonged time, and the ^{13}C-NMR spectrum could not be recorded. Instead, it was immediately suspended in *o*-dichlorobenzene (250 mL) and warmed slowly to 110°C for 15 min and then to 140°C for 1 h to give a red-brown solid. Filtration, recrystallization from *o*-dichlorobenzene, boiling in benzene for 1 h to remove the *o*-dichlorobenzene and finally drying overnight in a vacuum oven at 100°C gave 2,8-dinitro-3,4,9,10-bisfuroxanodibenzo-1,3a,4,6a-tetraazapentalene (15) as a red-brown powder (2.88 g, 50%), m.p. 248°C (dec). IR: 3060, 1660, 1590, 1550, 1540, 1410, 1330, 1300, 1260, 1200, 1120, 1070, 990, 890, 760, 750, 735 cm^{-1}. ^{1}H-NMR (DMSO): 9.74 (s). ^{13}C-NMR (DMSO): 145.87 ($C_{3,9}$), 135.46 ($C_{4a,10a}$), 132.13 ($C_{2,8}$), 120.72 ($C_{1,7}$), 114.40 ($C_{1a,7a}$), 106.51 ($C_{4,10}$). (Assignments are not unequivocal.) M/z: 414 (parent ion, discernible), 222 (base peak).

2,2,8,8-TETRAHYDROXY-1,7-DIOXO-3,4,9,10-BISFUROXANO- DIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (2,2,8,8-TETRA- HYDROXY-1,7-DIOXO-3,4,9,10-BISFUROXANO-5,11-DEHYDRO- 5*H*,11*H*-BENZOTRIAZOLO[2,1-*a*]BENZOTRIAZOLE) (9)

(a) Trifluoromethanesulfonic acid (8 mL) was placed in a 50-mL flask under an atmosphere of nitrogen, and 100% nitric acid (1.6 mL) was added dropwise and with stirring to form a white crystalline solid (nitronium trifluoromethanesulphonate). After thorough mixing, dichloromethane (5 mL) was added, followed by 2,8-dinitro-3,4,9,10-bisfuroxanodibenzo-1,3a,4,6a-tetra-azapentalene (15) (1.2 g, 0.29 mmol). The temperature was then raised slowly to 60 to 70°C, and maintained for 1 h. The mixture was cooled and quenched in ice water (600 mL). Filtration, washing with water, and drying at the pump gave red-brown solid (0.26 g; 21%); recrystallization from acetonitrile (400 mL reduced to 50 mL) gave 2,2,8,8-tetrahydroxy-1,7-dioxo-3,4,9,10-bisfuroxanodibenzo-1,3a,4,6a-tetraazapentalene (9) as a salmon-red colored solid (0.12 g), m.p.

326°C (dec) (endotherm at 163°C; loss of water?). IR: 3200 (very broad), 1740, 1670, 1650, 1550, 1500, 1480, 1380, 1360, 1250, 1080, 1030, 1000, 900, 800, 780 cm^{-1}. ^{13}C-NMR (DMSO): 167.63 ($C_{1,7}$), 164.50 ($C_{2,8}$), 150.33 ($C_{3,9}$), 138.49 ($C_{4a,10a}$), 114.88 ($C_{1a,7a}$), 104.04 ($C_{4,10}$).

(b) One hundred percent nitric acid (10 mL) was placed in a 25-mL flask and cooled to 0°C under an atmosphere of nitrogen. 2,8-Dinitro-3,4,9,10-bisfuroxanodibenzo-1,3a,4,6a-tetraazapentalene (**15**) (0.10 g, 0.02 mmol) was added with stirring, followed by Nafion NR50 beads (0.10 g). The reaction mixture was allowed to warm to ambient temperature, and was stirred for 24 h to give a clear red solution, which was decanted off the Nafion beads and evaporated under reduced pressure to remove the nitric acid and leave a quantitative yield (0.10 g) of a clean red solid, identified by its IR spectrum as 2,2,8,8-tetrahydroxy-1,7-dioxo-3,4,9,10-bisfuroxanodibenzo-1,3a,4,6a-tetraazapentalene (**9**). The reaction was unchanged when dinitrogen pentoxide (0.10 g) was added to the cold nitric acid to trap any water generated in the reaction.

1,2,7,8-TETRADIOXO-3,4,9,10-BISFUROXANODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (1,2,7,8-TETRADIOXO-3,4,9,10-BISFUROXANO-5,11-DEHYDRO-5*H*,11*H*-BENZO-TRIAZOLO[2,1-*a*]BENZOTRIAZOLE) (10)

2,2,8,8-Tetrahydroxy-1,7-dioxo-3,4,9,10-bisfuroxanodibenzo-1,3a,4,6a-tetraazapentalene (**9**) (0.10 g) was placed on a watch glass and heated in a vacuum oven at 105°C for 24 h to give an ochre powder (0.09 g), identified as 1,2,7,8-tetraoxo-3,4,9,10-bisfuroxanodibenzo-1,3a,4,6a-tetraazapentalene (**10**), m.p. 326°C (dec). IR: 1725, 1675, 1640, 1620, 1490, 1465, 1380, 1325, 1075, 1050, 970, 895 cm^{-1}. ^{13}C-NMR (DMSO): 166.28 ($C_{1,7}$), 164.33 ($C_{2,8}$), 144.06 ($C_{3,9}$), 140.34 ($C_{4a,10a}$), 115.65 ($C_{1a,7a}$), 107.54 ($C_{4,10}$).

o-NITROSONITROBENZENE

o-Nitroaniline (13.8 g, 100 mmol) was added to dichloromethane (300 mL) and 6 N sulfuric acid (1200 mL). Potassium persulfate (108 g, 400 mmol) was added, and the reaction mixture was heated under reflux with stirring for 20 h. The organic phase was separated, concentrated to 150 mL, and purified by column chromatography on silica (210 g, 45 x 340 millimeter (mm)) using dichloromethane as eluent, giving *o*-nitrosonitrobenzene as a green solid (6.14 g, 40%), m.p. 122 to 124°C (lit. 126°C (Reference 17)). ^{1}H-NMR spectrum in CDCl$_3$ at ambient temperature showed approximately 60% *o*-nitrosonitrobenzene and 40% dimer; heating to 318 K (46°C) caused dissociation of the dimer and simplification of the spectrum: 8.08 (d, J = 8.0 Hz, 1 H, H$_6$), 7.83 (apparent t, J = 8.0 Hz, 1 H), 7.67 (apparent t, J = 8.0 Hz, 1 H), 6.52 (d, J = 8.0 Hz, 1 H, H$_3$).

2-tert-BUTYL-1-(2-NITROPHENYL)-DIAZENE-1-OXIDE (20)

o-Nitrosonitrobenzene (10.0 g, 65.7 mmol) was added to a solution of dibromo-tert-butylamine (15.2 g, 65.7 mmol) in dichloromethane (200 mL). The reaction mixture was stirred at ambient temperature for 2 h, and evaporated to dryness under reduced pressure. The residue was dissolved in chloroform (100 mL) and purified by column chromatography on silica (750 g, 95 x 245 mm) using chloroform as eluent, giving a brown oily product (13.9 g, 94%) identified by ^{1}H-NMR as 2-tert-butyl-1-(2-nitrophenyl)-diazene-1-oxide (**20**). ^{1}H-NMR (CDCl$_3$): 7.94 (dd, J = 8.08, 1.32 Hz, 1 H, H$_6$), 7.75 (dd, J = 7.96, 1.76 Hz, 1 H, H$_3$), 7.70 (ddd, J = 7.96, 7.20, 1.32 Hz, 1 H, H$_4$), 7.59 (ddd, J = 8.08, 7.20, 1.76 Hz, 1 H, H$_5$), 1.42 (s, 9 H, C(CH$_3$)$_3$).

2-tert-BUTYL-1-(2-ANILINO)-DIAZENE-1-OXIDE (21)

2-tert-Butyl-1-(2-nitrophenyl)-diazene-1-oxide (**20**) (13.88 g, 65.7 mmol) was dissolved in a mixture of ethanol (50 mL) and ethyl acetate (50 mL), and stannous chloride dihydrate (49.08 g, 218 mmol) was added with stirring at ambient temperature. The reaction is mildly exothermic, but the temperature was maintained at ca. 30°C for 3.5 h. The reaction mixture was poured onto a chromatography column loaded with alumina (630 g, 45 x 450 mm) and eluted with ethyl acetate. The product was concentrated to 50 mL and poured onto a second column of alumina (630 g, 45 x 450 mm) and again eluted with ethyl acetate to give a brown oil (12.0 g). This product was dissolved in chloroform (75 mL) and purified on a silica column (1000 g, 95 x 340 mm) using chloroform as eluent, giving a yellow oily product (9.19 g, 76%) identified by ^{1}H-NMR as 2-tert-butyl-1-(2-anilino)-diazene-1-oxide (**21**). ^{1}H-NMR (CDCl$_3$): 8.01 (dd, J = 8.80, 1.40 Hz, 1 H, H$_6$), 7.26 (ddd, J = 8.20, 7.16, 1.40 Hz, 1 H, H$_4$), 6.94 (dd, J = 8.20, 1.20 Hz, 1 H, H$_3$), 6.83 (ddd, J = 8.80, 7.16, 1.20 Hz, 1 H, H$_5$), 5.99 (br s, 2 H, NH$_2$), 1.50 (s, 9 H, C(CH$_3$)$_3$). A much smaller fraction was eluted with 5% ethyl acetate in chloroform, and evaporated to give a red-brown solid. Extraction with hot hexane (50 mL) and cooling gave dark crystals identified as 2,2'-diaminoazoxybenzene (2-azoxyaniline) (0.041 g), m.p. 113-4°C (lit. 115°C (Reference 24)). ^{1}H-NMR (CDCl$_3$): 8.41 (dd, J = 8.24, 1.40 Hz, 1 H), 7.96 (dd, J = 8.32, 1.52 Hz, 1 H), 7.26 (ddd, J = 8.24, 7.12, 1.52 Hz, 1 H), 7.17 (ddd, J = 8.32, 7.20. 1.40 Hz, 1 H), 6.81 (complex multiplet (overlapping signals), 2 H), 6.76 (complex multiplet (overlapping signals), 2 H), 5.0 (br s, 4 H, NH$_2$'s). M/z: 228 (parent ion), 210, 122, 106, 92 (base peak).

5,7-DINITROBENZO-1,2,3,4-TETRAZINE-1,3-DIOXIDE (18)

2-tert-Butyl-1-(2-anilino)-diazene-1-oxide (**21**) (0.85 g, 4.4 mmol) was dissolved in dichloromethane (25 mL), and dinitrogen pentoxide (2.7 g, 25 mmol)

was added at -20°C under an atmosphere of nitrogen. The temperature was allowed to rise slowly to 0°C, and the dinitrogen pentoxide dissolved to give a burgundy-colored solution. After 15 min at 0°C, the solution had become pale orange, and a solution of 100% nitric acid (4 mL, 95 mmol) in 20% oleum (6 mL) was added to give a two-phase system. The mixture was stirred and the color went from the dichloromethane to the acid phase without noticeable exotherm. The reaction mixture was heated to 80°C, with the dichloromethane distilling away, and held at that temperature for 2 h. Cooling, quenching on ice, filtration, washing with water, and drying at the pump gave a yellow solid (0.88 g, 79%). Recrystallization from dichloroethane gave 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (18) (0.66 g) as yellow needles, m.p. 205-207°C (dec) (lit. 209-211°C (Reference 14)). IR: 3100, 1620, 1600, 1540, 1520, 1470, 1440, 1430, 1340, 1180, 1080, 990, 940, 920, 860, 750, 730, 690, 660 cm^{-1}. ^{1}H-NMR (acetone): 9.42 (d, J = 2.40 Hz, 1 H, H_8), 9.32 (d, J = 2.40 Hz, 1 H, H_6). ^{13}C-NMR (acetone): 147.15 (C_7), 142.88 (C_5), 140.88 (C_{4a}), 129.88 (C_{1a}), 128.05 (C_6), 120.01 (C_8). M/z: 254 (parent ion), 210, 209, 181, 150, 120, 87, 74 (base peak), 62, 61.

SINGLE-CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 2,4,8,10-TETRANITRODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (TACOT) (3), 4,10-BIS(ACETAMIDO)-2,8-DINITRODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (13), AND 5,7-DINITROBENZO-1,2,3,4-TETRAZINE-1,3-DIOXIDE (18)

Data collections were carried out on an automated Siemens diffractometer equipped with an incident-beam monochrometer. Space group assignments were based on systematic absences present in the diffraction patterns, and were confirmed by structure solution and refinement. All structures were initially determined by direct methods, aided by the program XS, and refined with the full-matrix least squares program XLS, contained in the SHELXTL collection of computer programs (Reference 25).

Crystal Data (3)

$C_{12}H_4N_8O_8$, F.W. = 388.23, crystallizes in the orthorhombic space group P_{bca}, with a = 8.589(3), b = 11.452(2), c = 14.327(3) Å, Vol = 1409.2(6) Å^3, Z = 4, and Dens (X-ray) = 1.830 g/cm^3. A dark orange 0.55 x 0.45 x 0.05 mm crystal, in the shape of a clear plate was used, with MoKα radiation, λ = 0.71073 Å, at T = 293(2) K. The refinement agreement factors were R = 0.0684, wR2 = 0.0870 for all (none considered unobservable) 1243 unique reflections.

Crystal Data (13)

$C_{16}H_{12}N_8O_6$ + 2 C_2H_6SO (DMSO solvate), F.W. = 568.59, crystallizes in the monoclinic space group P2$_1$/c, with a = 5.3095(5), b = 12.8082(7), c = 19.182 (2) Å, β = 98.845(7)°, Vol = 1289 0(2) Å^3, Z = 2, and Dens (X-ray) = 1.465 g/cm^3. A red-orange 0.05 x 0.06 x 0.70 mm acicular prism was used, with CuKα radiation, λ = 1.54178 Å at T = 223(2) K. The refinement agreement factors were R = 0.0732, wR2 = 0.1264 for all (none considered unobserved) 1727 unique reflections.

Crystal Data (18)

$C_6H_2N_6O_6$, F.W. = 254.14, crystallizes in the orthorhombic space group Pca2$_1$, with a = 9.9592(11), b = 17.940(2), c = 10.3121(13) Å, Vol = 1842.5(4) Å^3, Z = 8 and Dens (X-ray) = 1.832 g/cm^3. A yellow 0.07 x 0.36 x 0.43 mm crystal in the shape of a thick plate was used, with CuKα radiation, λ = 1.54178 Å, at T = 294(2) K. The refinement agreement factors were R = 0.0562, wR2 = 0.1029 for all (none considered unobserved) 1362 unique reflections.

Detailed results of the X-ray diffraction analyses are included in the Appendix.

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Appendix

DETAILS OF SINGLE CRYSTAL X-RAY STRUCTURE ANALYSIS OF 2,4,8,10-TETRANITRODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (TACOT) (**3**), 4,10-BIS(ACETAMIDO)-2,8-DINITRODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (**13**), AND 5,7-DINITROBENZO-1,2,3,4-TETRAZINE-1,3-DIOXIDE (**18**).
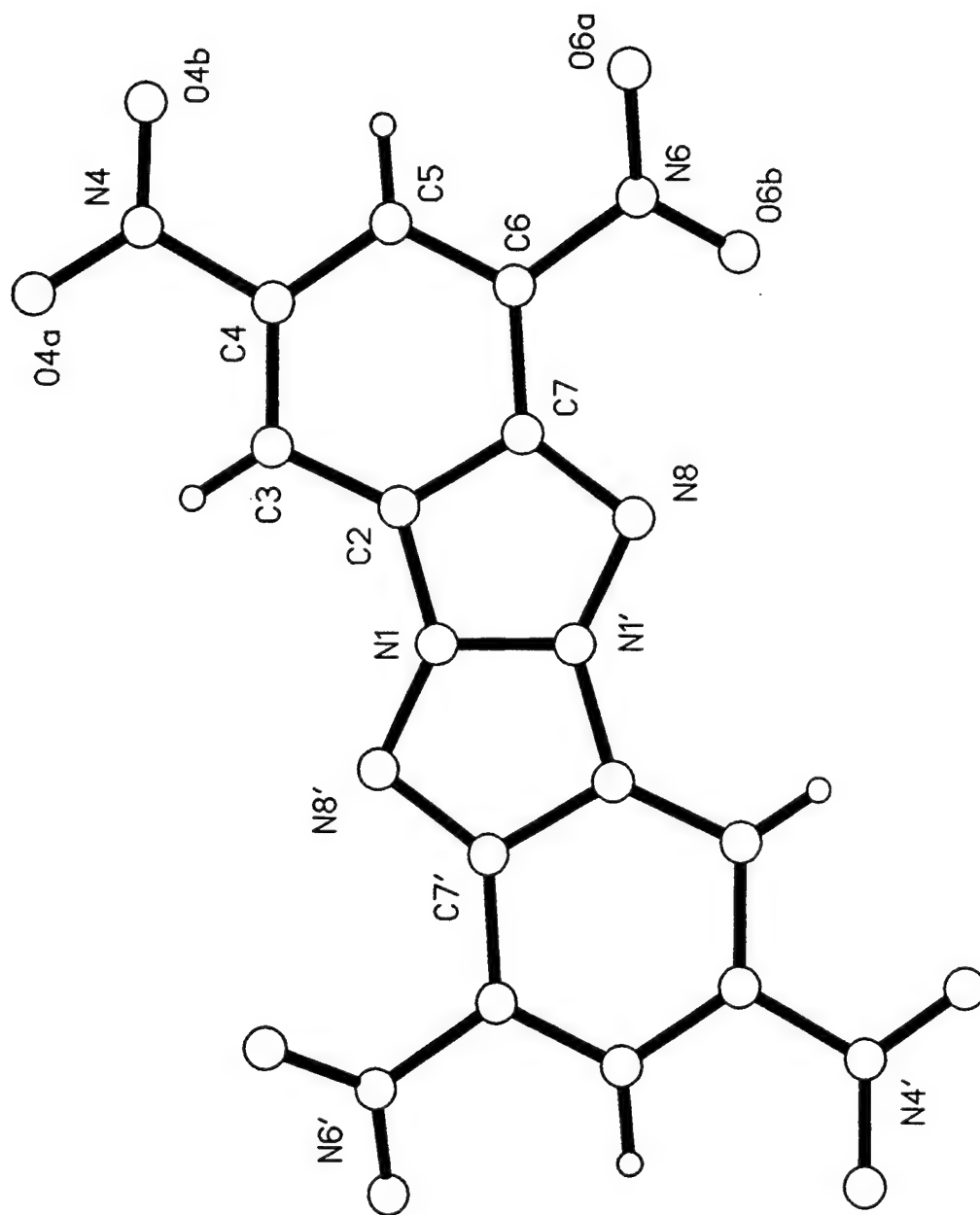
FIGURE A-1. Molecular Structure of 2,4,8,10-Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (TACOT) (3).
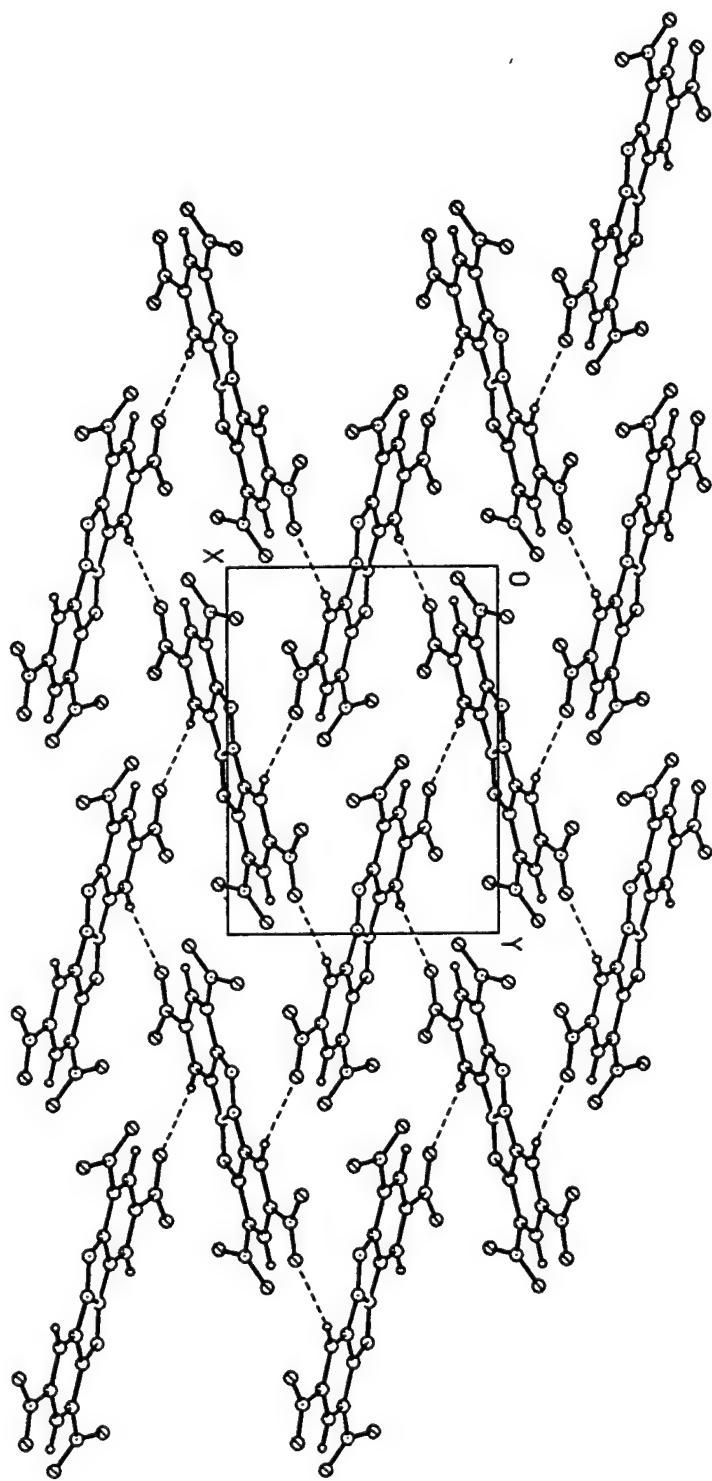
FIGURE A-2. Molecular Assembly of 2,4,8,10-Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (TACOT) (**3**) in the Crystal.
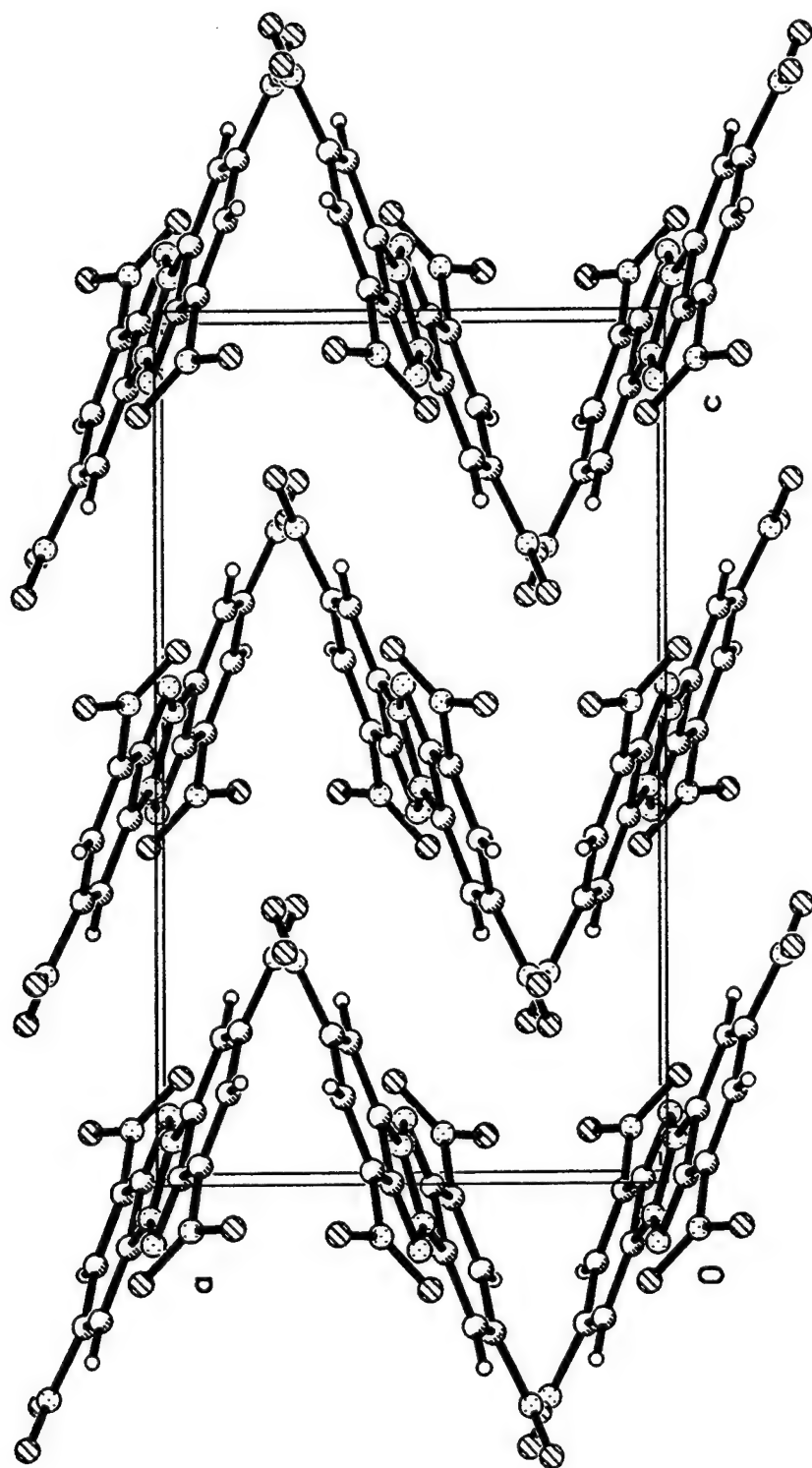
FIGURE A-3. Molecular Assembly of 2,4,8,10-Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (TACOT) (3) in the Crystal.
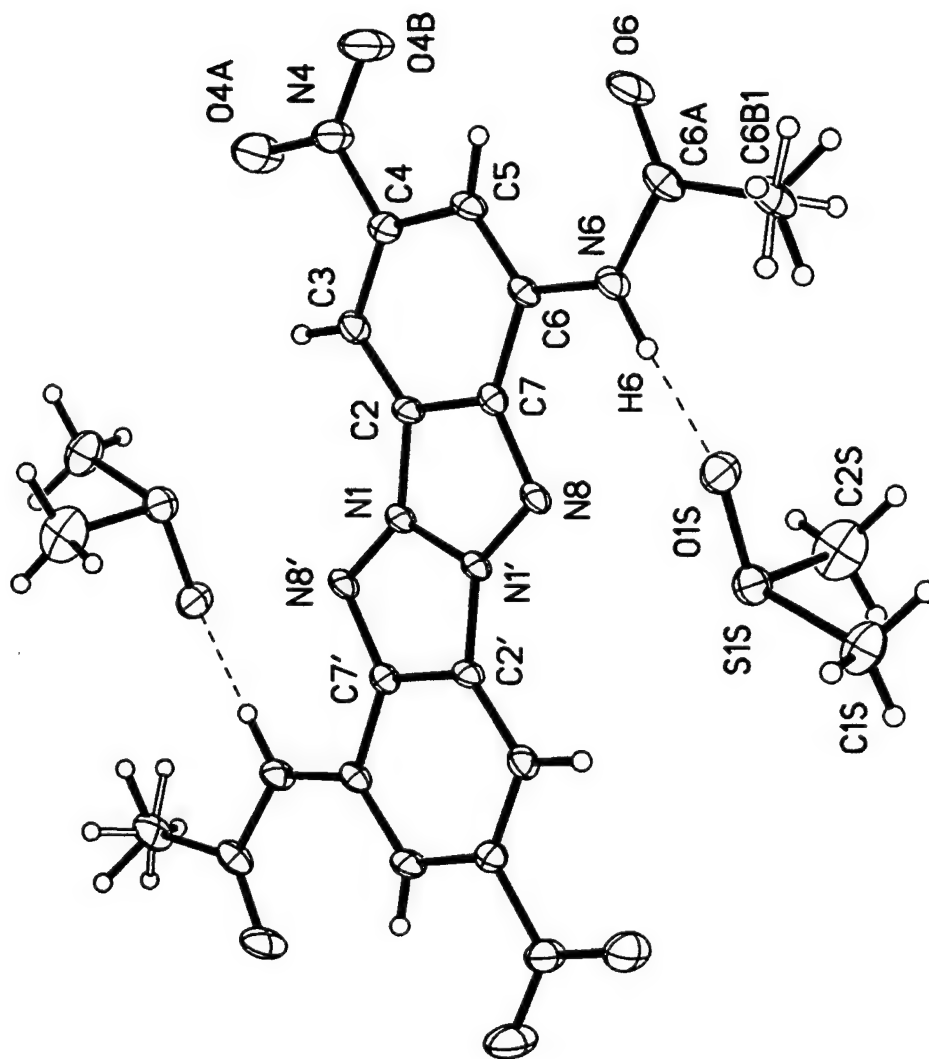
FIGURE A-4. Molecular Structure of 4,10-Bis(acetamido)-2,8-dinitrodibenzo-1,3a,4,6a-tetraazapentalene (**13**).
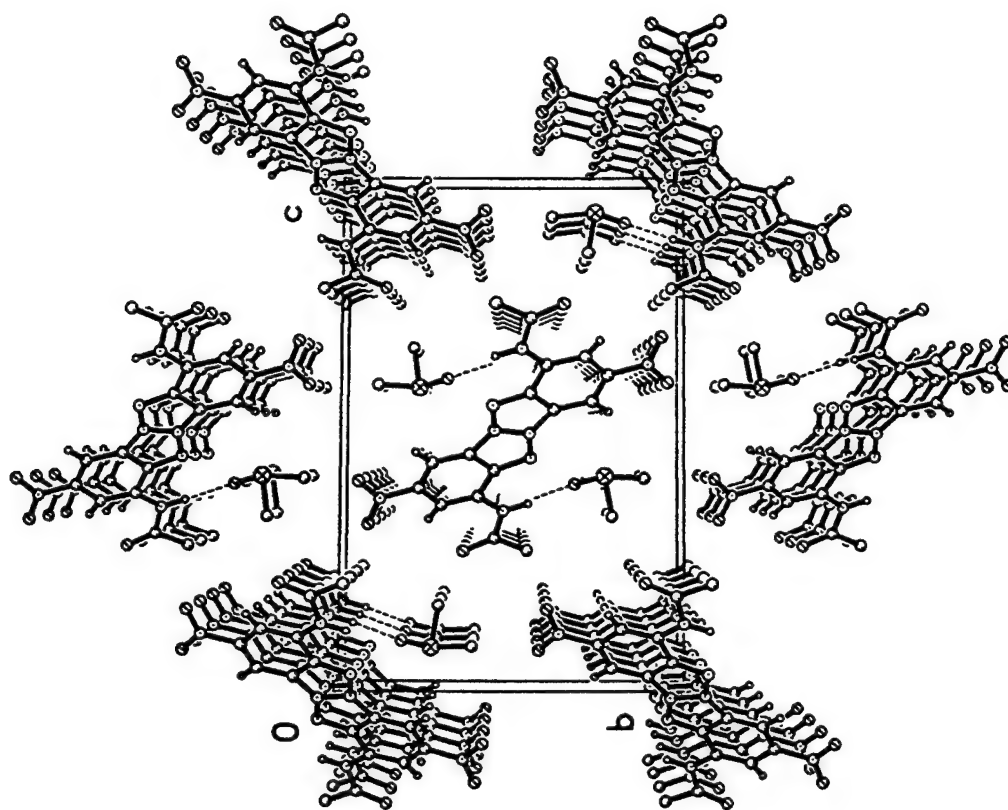
FIGURE A-5. Molecular Assembly of 4,10-Bis(acetamido)-2,8-dinitrodibenzo-1,3a,4,6a-tetraazapentalene (**13**) in the Crystal.
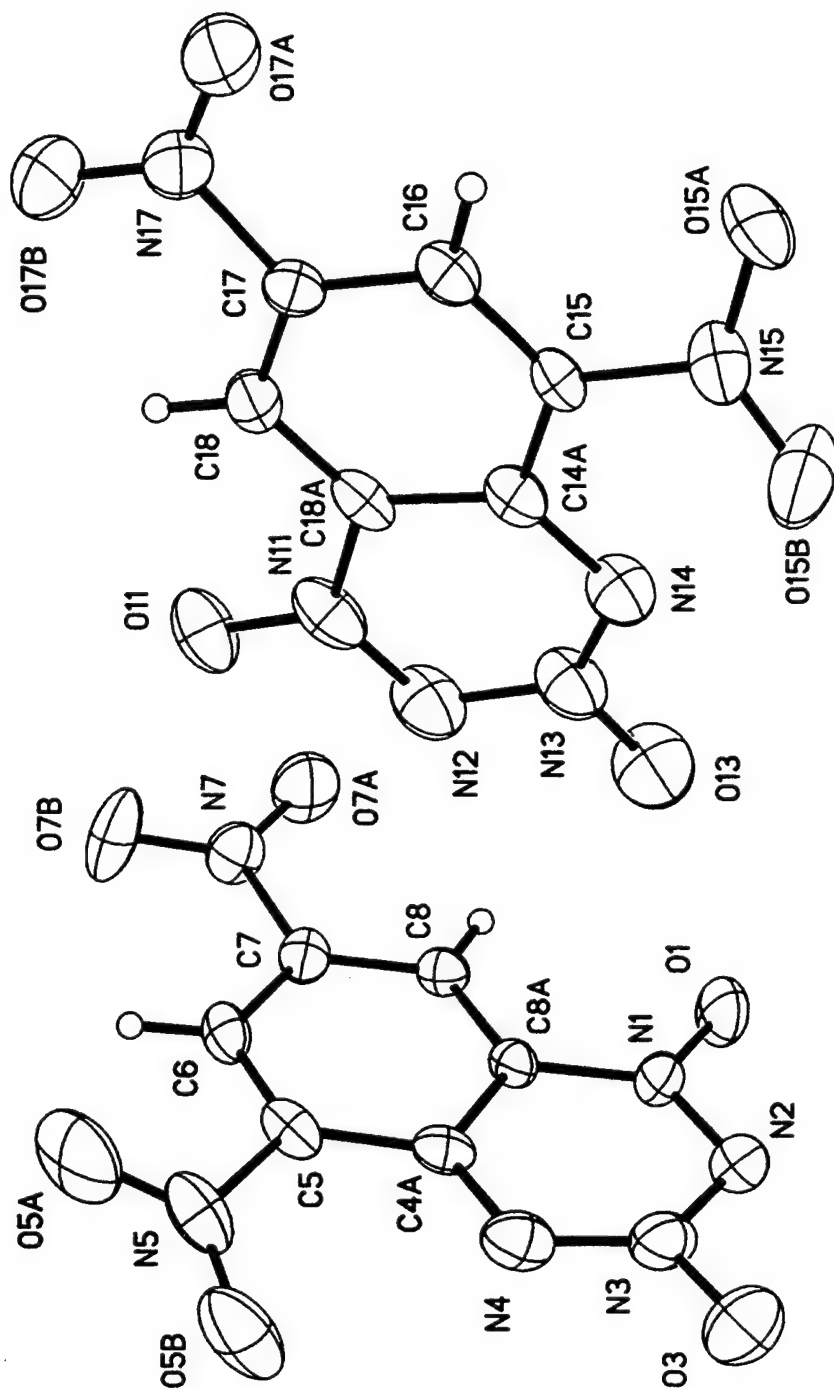
FIGURE A-6. Molecular Structure of 5,7-Dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (18), Showing the Two Distinct Molecules in the Asymmetric Unit.

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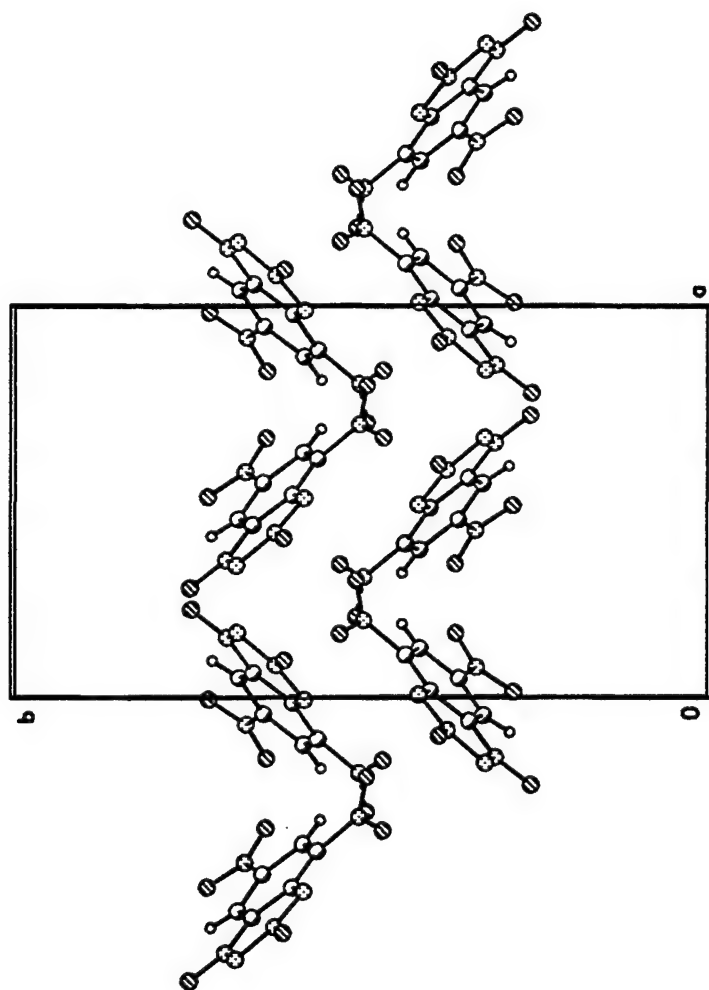
FIGURE A-7. Assembly of 5,7-Dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide Molecules **18A**, Showing "Double Pleated Sheet."
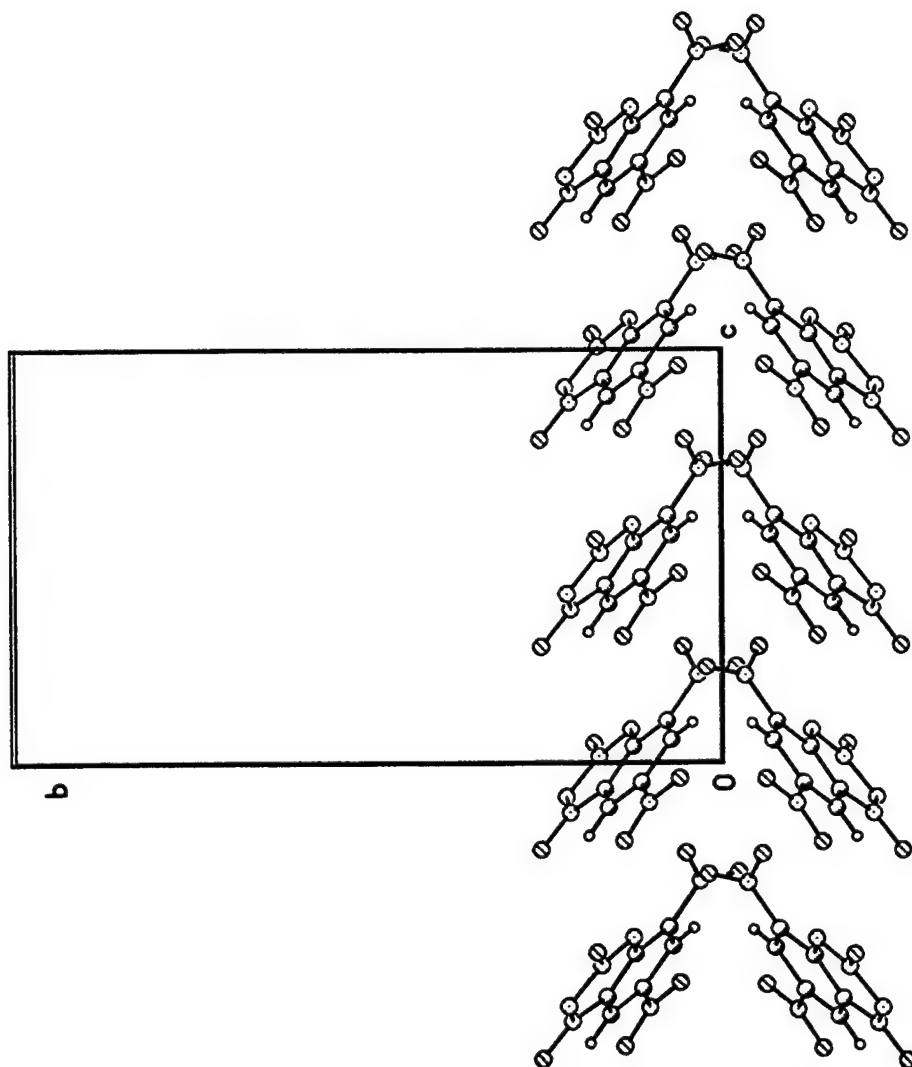
FIGURE A-8. Assembly of 5,7-Dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide Molecules **18B**, Showing Herringbone Structure.

TABLE A-1. Crystal Data and Structure Refinement for 3.

|	
Identification code	tacot
Empirical formula	$C_{12}H_4N_8O_8$
Formula weight	388.23
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 8.589(3) Å alpha = 90^0
	b = 11.452(2) Å beta = 90^0
	c = 14.327(3) Å gamma = 90^0
Volume, Z	1409.2(6) $Å^3$, 4
Density (calculated)	1.830 Mg/m^3
Absorption coefficient	0.158 mm^{-1}
F(000)	784
Crystal size	0.55 x 0.45 x 0.05 mm
θ range for data collection	2.84 to 25.03^0
Limiting indices	$-1 \leq h \leq 10, -1 \leq k \leq 13, -1 \leq l \leq 17$
Reflections collected	1753
Reflections 'observed'	886 [I>2sigma(I)]
Independent reflections	1243 (R_{int} = 0.0223)
Absorption correction	None
Max. and min. transmission	na? and na
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1243 / 0 / 136
Goodness-of-fit on F^2	1.042
Final R indices [I>2σ(I)]	R1 = 0.0397, wR2 = 0.0752
R indices (all data)	R1 = 0.0684, wR2 = 0.0870
Extinction coefficient	0.0039(6)
Largest diff. peak and hole	0.195 and -0.200 $eÅ^{-3}$

TABLE A-2. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) for **3**. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	214(2)	5091(2)	-451(1)	27(1)
C(2)	640(3)	4014(2)	-800(2)	27(1)
C(3)	1217(3)	3695(2)	-1666(2)	30(1)
C(4)	1566(3)	2525(2)	-1755(2)	29(1)
N(4)	2293(3)	2113(2)	-2616(2)	39(1)
O(4A)	2702(2)	2842(2)	-3192(1)	50(1)
O(4B)	2472(3)	1062(2)	-2712(1)	68(1)
C(5)	1344(3)	1715(2)	-1046(2)	31(1)
C(6)	787(3)	2061(2)	-198(2)	28(1)
N(6)	619(3)	1187(2)	536(1)	32(1)
O(6A)	1449(2)	317(1)	500(1)	43(1)
O(6B)	-343(2)	1369(2)	1152(1)	46(1)
C(7)	399(3)	3248(2)	-42(2)	27(1)
N(8)	-139(2)	3795(2)	737(1)	30(1)

	x	y	z	U(iso)
H(3)	1380(29)	4219(20)	-2136(17)	33(7)
H(5)	1591(26)	916(20)	-1174(15)	21(6)

TABLE A-3. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **3**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^*b^* U_{12}]$.

	U11	U22	U33	U23	U13	U12
N(1)	31(1)	21(1)	29(1)	-1(1)	0(1)	0(1)
C(2)	30(1)	20(1)	31(1)	-3(1)	-2(1)	0(1)
C(3)	30(1)	29(1)	31(1)	2(1)	-1(1)	0(1)
C(4)	31(1)	29(1)	28(1)	-3(1)	1(1)	3(1)
N(4)	45(2)	40(1)	30(1)	-1(1)	-1(1)	14(1)
O(4A)	56(1)	54(1)	39(1)	6(1)	14(1)	10(1)
O(4B)	119(2)	40(1)	45(1)	-6(1)	10(1)	33(1)
C(5)	32(2)	23(1)	37(2)	-4(1)	-1(1)	3(1)
C(6)	30(1)	23(1)	30(1)	2(1)	-3(1)	-2(1)
N(6)	38(1)	24(1)	35(1)	0(1)	-2(1)	0(1)
O(6A)	57(1)	25(1)	47(1)	4(1)	-2(1)	11(1)
O(6B)	52(1)	39(1)	47(1)	6(1)	18(1)	3(1)
C(7)	25(1)	26(1)	31(1)	-1(1)	0(1)	-2(1)
N(8)	37(1)	20(1)	34(1)	-1(1)	2(1)	0(1)

TABLE A-4. Bond Lengths (Å) and Angles (°) for **3**.

N(1)-N(8)#1	1.341(3)	N(1)-N(1)#1	1.361(4)
N(1)-C(2)	1.380(3)	C(2)-C(3)	1.385(3)
C(2)-C(7)	1.411(3)	C(3)-C(4)	1.379(3)
C(4)-C(5)	1.388(3)	C(4)-N(4)	1.461(3)
N(4)-O(4B)	1.222(3)	N(4)-O(4A)	1.225(3)
C(5)-C(6)	1.364(3)	C(6)-C(7)	1.417(3)
C(6)-N(6)	1.459(3)	N(6)-O(6A)	1.226(3)
N(6)-O(6B)	1.227(3)	C(7)-N(8)	1.360(3)
N(8)-N(1)#1	1.341(3)		
N(8)#1-N(1)-N(1)#1	115.0(2)	N(8)#1-N(1)-C(2)	138.8(2)
N(1)#1-N(1)-C(2)	106.2(2)	N(1)-C(2)-C(3)	130.9(2)
N(1)-C(2)-C(7)	103.8(2)	C(3)-C(2)-C(7)	125.3(2)
C(4)-C(3)-C(2)	114.6(2)	C(3)-C(4)-C(5)	123.5(2)
C(3)-C(4)-N(4)	118.9(2)	C(5)-C(4)-N(4)	117.4(2)
O(4B)-N(4)-O(4A)	124.0(2)	O(4B)-N(4)-C(4)	117.8(2)
O(4A)-N(4)-C(4)	118.2(2)	C(6)-C(5)-C(4)	120.3(2)
C(5)-C(6)-C(7)	120.1(2)	C(5)-C(6)-N(6)	118.5(2)
C(7)-C(6)-N(6)	121.4(2)	O(6A)-N(6)-O(6B)	124.0(2)
O(6A)-N(6)-C(6)	118.0(2)	O(6B)-N(6)-C(6)	118.0(2)
N(8)-C(7)-C(2)	113.3(2)	N(8)-C(7)-C(6)	130.6(2)
C(2)-C(7)-C(6)	116.1(2)	N(1)#1-N(8)-C(7)	101.8(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

TABLE A-5. Crystal Data and Structure Refinement for **13**.

Identification code	wils11tt
Empirical formula	$C_{20}H_{24}N_8O_8S_2$
Formula weight	568.59
Temperature	223(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 5.3095(5) Å alpha = 90^0
	b = 12.8082(7) Å beta = $98.845(7)^0$
	c = 19.182(2) Å gamma = 90^0
Volume, Z	1289.0(2) $Å^3$, 2
Density (calculated)	1.465 Mg/m^3
Absorption coefficient	2.416 mm^{-1}
F(000)	592
Crystal size	.05 x .06 x .7 mm
θ range for data collection	4.17 to 56.95^0
Limiting indices	$-5 \le h \le 5$, $-13 \le k \le 13$, $0 \le l \le 20$
Reflections collected	3585
Reflections 'observed'	1227 [I>2sigma(I)]
Independent reflections	1727 (R_{int} = 0.0470)
Absorption correction	Integration
Max. and min. transmission	0.8980 and 0.4764
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1726 / 0 / 187
Goodness-of-fit on F^2	1.036
Final R indices [I>2σ(I)]	R1 = 0.0475, wR2 = 0.1100
R indices (all data)	R1 = 0.0732, wR2 = 0.1264
Extinction coefficient	0.0015(4)
Largest diff. peak and hole	0.214 and -0.269 $eÅ^{-3}$

TABLE A-6.   Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3) for **13**. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	5560(5)	4524(2)	5029(1)	31(1)
C(2)	4024(6)	3860(3)	4590(2)	29(1)
C(3)	4248(7)	2822(3)	4437(2)	34(1)
C(4)	2242(6)	2438(3)	3968(2)	36(1)
N(4)	2310(6)	1341(3)	3775(2)	48(1)
O(4A)	3951(6)	783(3)	4099(2)	81(1)
O(4B)	740(6)	1004(3)	3297(2)	78(1)
C(5)	127(7)	3039(3)	3648(2)	35(1)
C(6)	-42(6)	4075(3)	3801(2)	30(1)
N(6)	-1984(5)	4756(3)	3520(2)	36(1)
C(6A)	-4004(6)	4515(4)	2996(2)	40(1)
O(6)	-4342(5)	3645(3)	2749(1)	55(1)
C(7)	1979(6)	4510(3)	4294(2)	29(1)
N(8)	2220(5)	5515(2)	4524(1)	32(1)
C(6B1)	-5687(7)	5430(4)	2752(2)	51(1)
C(6B2)	-5687(7)	5430(4)	2752(2)	51(1)
S(1S)	-731(2)	7699(1)	4139(1)	46(1)
O(1S)	-2673(5)	6851(2)	3978(1)	48(1)
C(1S)	-2501(8)	8884(4)	4091(3)	65(1)
C(2S)	598(9)	7892(5)	3360(3)	80(2)

	x	y	z	U(iso)
H(3)	5664(67)	2376(30)	4629(18)	41
H(5)	-982(65)	2676(30)	3374(19)	42
H(6)	-1939(66)	5457(32)	3655(19)	43
H(6BC)	-4743(49)	6073(4)	2859(40)	62
H(6BA)	-7165(79)	5425(37)	2993(33)	62
H(6BB)	-6238(129)	5380(34)	2247(7)	62
H(6BD)	-5014(3)	5790(32)	2376(25)	72
H(6BE)	-5735(173)	5905(26)	3143(9)	72
H(6BE)	-7397(38)	5184(5)	2580(33)	72
H(1SC)	-1338(9)	9473(4)	4130(14)	78
H(1SA)	-3498(38)	8908(10)	4475(8)	78
H(1SB)	-3633(36)	8918(10)	3644(6)	78
H(2S1)	1532(54)	8546(13)	3393(8)	96
H(2S2)	-755(10)	7916(27)	2958(3)	96
H(2S3)	1747(50)	7321(14)	3301(10)	96

TABLE A-7. Bond Lengths (Å) and Angles (°) for **13.**

N(1)-N(8)#1	1.347(3)	N(1)-N(1)#1	1.353(5)
N(1)-C(2)	1.374(4)	C(2)-C(3)	1.370(5)
C(2)-C(7)	1.416(5)	C(3)-C(4)	1.375(5)
C(4)-C(5)	1.421(5)	C(4)-N(4)	1.455(5)
N(4)-O(4B)	1.219(4)	N(4)-O(4A)	1.221(4)
C(5)-C(6)	1.364(5)	C(6)-N(6)	1.395(5)
C(6)-C(7)	1.429(5)	N(6)-C(6A)	1.387(5)
C(6A)-O(6)	1.212(5)	C(6A)-C(6B2)	1.504(6)
C(6A)-C(6B1)	1.504(6)	C(7)-N(8)	1.361(4)
N(8)-N(1)#1	1.347(3)	S(1S)-O(1S)	1.497(3)
S(1S)-C(2S)	1.764(5)	S(1S)-C(1S)	1.780(4)
N(8)#1-N(1)-N(1)#1	114.6(3)	N(8)#1-N(1)-C(2)	138.2(3)
N(1)#1-N(1)-C(2)	107.2(3)	C(3)-C(2)-N(1)	132.0(3)
C(3)-C(2)-C(7)	124.8(3)	N(1)-C(2)-C(7)	103.2(3)
C(2)-C(3)-C(4)	113.7(3)	C(3)-C(4)-C(5)	124.7(4)
C(3)-C(4)-N(4)	117.7(3)	C(5)-C(4)-N(4)	117.5(3)
O(4B)-N(4)-O(4A)	121.9(4)	O(4B)-N(4)-C(4)	119.5(3)
O(4A)-N(4)-C(4)	118.6(3)	C(6)-C(5)-C(4)	120.5(3)
C(5)-C(6)-N(6)	126.5(3)	C(5)-C(6)-C(7)	117.0(3)
N(6)-C(6)-C(7)	116.5(3)	C(6A)-N(6)-C(6)	125.7(4)
O(6)-C(6A)-N(6)	122.6(4)	O(6)-C(6A)-C(6B2)	123.3(3)
N(6)-C(6A)-C(6B2)	114.1(4)	O(6)-C(6A)-C(6B1)	123.3(3)
N(6)-C(6A)-C(6B1)	114.1(4)	N(8)-C(7)-C(2)	113.4(3)
N(8)-C(7)-C(6)	127.4(3)	C(2)-C(7)-C(6)	119.2(3)
N(1)#1-N(8)-C(7)	101.6(3)	O(1S)-S(1S)-C(2S)	106.2(2)
O(1S)-S(1S)-C(1S)	105.5(2)	C(2S)-S(1S)-C(1S)	96.6(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

TABLE A-8. Anisotropic Displacement Parameters (Å^2 x 10^3) for **13**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [(ha*)^{2}U$_{11}$ + ... + 2hka*b*U$_{12}$].

	U11	U22	U33	U23	U13	U12
N(1)	25(2)	33(2)	30(2)	0(2)	-10(1)	2(1)
C(2)	23(2)	32(2)	30(2)	-3(2)	-6(2)	-2(2)
C(3)	30(2)	39(3)	31(2)	1(2)	-3(2)	3(2)
C(4)	35(2)	33(2)	36(2)	-1(2)	-2(2)	-1(2)
N(4)	46(2)	39(2)	55(2)	-11(2)	-7(2)	2(2)
O(4A)	85(2)	49(2)	93(3)	-19(2)	-35(2)	26(2)
O(4B)	68(2)	51(2)	100(3)	-26(2)	-33(2)	0(2)
C(5)	27(2)	41(3)	33(2)	-4(2)	-7(2)	-5(2)
C(6)	19(2)	40(3)	28(2)	-1(2)	-4(2)	-1(2)
N(6)	27(2)	41(2)	36(2)	-4(2)	-8(1)	4(2)
C(6A)	25(2)	60(3)	32(2)	-3(2)	-1(2)	3(2)
O(6)	39(2)	63(2)	55(2)	-20(2)	-20(1)	5(2)
C(7)	24(2)	34(2)	28(2)	1(2)	-1(2)	2(2)
N(8)	26(2)	38(2)	27(2)	1(1)	-9(1)	3(1)
C(6B1)	32(2)	69(3)	47(2)	-3(2)	-15(2)	9(2)
C(6B2)	32(2)	69(3)	47(2)	-3(2)	-15(2)	9(2)
S(1S)	41(1)	43(1)	51(1)	2(1)	-6(1)	6(1)
O(1S)	38(2)	41(2)	61(2)	3(1)	-3(1)	1(1)
C(1S)	71(3)	45(3)	81(3)	6(3)	17(3)	13(2)
C(2S)	69(3)	82(4)	99(4)	7(3)	46(3)	6(3)

TABLE A-9. Crystal Data and Structure Refinement for **18**.

Identification code	wils10
Empirical formula	$C_6H_2N_6O_6$
Formula weight	254.14
Temperature	294(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	$a = 9.9592(11)$ Å alpha = 90°
	$b = 17.940(2)$ Å beta = 90°
	$c = 10.3121(13)$ Å gamma = 90°
Volume, Z	1842.5(4) $Å^3$, 8
Density (calculated)	1.832 Mg/m^3
Absorption coefficient	1.477 mm^{-1}
F(000)	1024
Crystal size	0.07 x 0.36 x 0.43 mm
θ range for data collection	2.46 to 57.77^o
Limiting indices	$-10 \le h \le 0$, $-8 \le k \le 19$, $0 \le l \le 11$
Reflections collected	2201
Reflections 'observed'	1112 [I>2sigma(I)]
Independent reflections	1362 (R_{int} = 0.0231)
Absorption correction	Integration
Max. and min. transmission	0.8859 and 0.6066
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1362 / 0 / 337
Goodness-of-fit on F^2	1.090
Final R indices [I>2σ(I)]	R1 = 0.0419, wR2 = 0.0937
R indices (all data)	R1 = 0.0562, wR2 = 0.1029
Absolute structure parameter	0.3(6)
Extinction coefficient	0.0012(3)
Largest diff. peak and hole	0.143 and -0.160 $eÅ^{-3}$

TABLE A-10. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3) for **18**. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	-1505(5)	3059(3)	5815(8)	56(1)
O(1)	-2220(4)	2550(2)	5371(8)	78(1)
N(2)	-1638(6)	3206(3)	7061(8)	70(2)
N(3)	-808(7)	3759(3)	7506(8)	76(2)
O(3)	-938(7)	3883(4)	8678(9)	125(2)
N(4)	85(6)	4177(3)	6856(8)	71(2)
C(4A)	168(5)	4008(3)	5588(8)	49(1)
C(5)	1093(6)	4364(3)	4754(9)	54(2)
N(5)	1964(7)	4969(3)	5228(10)	81(2)
O(5A)	2975(7)	5079(3)	4611(11)	134(3)
O(5B)	1629(7)	5317(3)	6166(9)	124(2)
C(6)	1250(5)	4159(3)	3504(9)	53(2)
C(7)	474(5)	3578(3)	3005(8)	51(2)
N(7)	750(6)	3323(3)	1686(8)	69(2)
O(7A)	112(6)	2789(3)	1310(8)	99(2)
O(7B)	1622(5)	3621(4)	1055(7)	112(2)
C(8)	-460(5)	3225(3)	3719(8)	46(1)
C(8A)	-598(5)	3432(3)	5000	44(1)
N(11)	3331(6)	2143(3)	3743(9)	78(2)
O(11)	3678(6)	2558(3)	2837(8)	100(2)
N(12)	2086(6)	2197(3)	4119(9)	90(2)
N(13)	1693(6)	1732(3)	5111(9)	85(2)
O(13)	508(5)	1797(3)	5423(10)	115(2)
N(14)	2479(6)	1277(3)	5778(8)	75(2)
C(14A)	3775(6)	1249(3)	5372(8)	54(2)
C(15)	4704(6)	767(3)	5996(8)	51(1)
N(15)	4343(6)	327(3)	7126(9)	75(2)
O(15A)	5031(7)	-223(3)	7331(10)	122(2)
O(15B)	3460(5)	526(4)	7818(9)	122(2)
C(16)	5979(6)	711(3)	5540(8)	56(2)
C(17)	6392(6)	1136(3)	4500(8)	53(2)
N(17)	7778(6)	1036(3)	4018(9)	72(2)
O(17A)	8484(5)	600(3)	4609(9)	104(2)
O(17B)	8106(6)	1392(3)	3077(8)	99(2)
C(18)	5562(7)	1606(4)	3888(8)	59(2)
C(18A)	4266(6)	1655(3)	4317(8)	56(2)

	x	y	z	U(iso)
H(6)	1851(50)	4405(29)	2923(59)	59
H(8)	-900(53)	2846(27)	3269(57)	51
H(16)	6628(54)	410(30)	5964(62)	61
H(18A)	5845(59)	1830(32)	3185(70)	64

TABLE A-11. Bond Lengths (Å) and Angles (°) for **18**.

N(1)-O(1)	1.244(6)	N(1)-N(2)	1.318(8)
N(1)-C(8A)	1.404(7)	N(2)-N(3)	1.371(8)
N(3)-O(3)	1.236(8)	N(3)-N(4)	1.342(8)
N(4)-C(4A)	1.345(8)	C(4A)-C(5)	1.413(8)
C(4A)-C(8A)	1.420(8)	C(5)-C(6)	1.350(9)
C(5)-N(5)	1.473(8)	N(5)-O(5B)	1.200(9)
N(5)-O(5A)	1.207(8)	C(6)-C(7)	1.396(8)
C(7)-C(8)	1.344(7)	C(7)-N(7)	1.461(8)
N(7)-O(7B)	1.210(7)	N(7)-O(7A)	1.214(7)
C(8)-C(8A)	1.379(8)	N(11)-O(11)	1.243(8)
N(11)-N(12)	1.302(8)	N(11)-C(18A)	1.409(8)
N(12)-N(13)	1.377(8)	N(13)-O(13)	1.230(7)
N(13)-N(14)	1.324(7)	N(14)-C(14A)	1.357(9)
C(14A)-C(18A)	1.398(8)	C(14A)-C(15)	1.421(8)
C(15)-C(16)	1.358(8)	C(15)-N(15)	1.453(8)
N(15)-O(15B)	1.188(8)	N(15)-O(15A)	1.220(7)
C(16)-C(17)	1.379(9)	C(17)-C(18)	1.340(9)
C(17)-N(17)	1.478(8)	N(17)-O(17B)	1.206(7)
N(17)-O(17A)	1.216(7)	C(18)-C(18A)	1.368(8)

O(1)-N(1)-N(2)	116.6(5)	O(1)-N(1)-C(8A)	119.8(5)
N(2)-N(1)-C(8A)	123.5(6)	N(1)-N(2)-N(3)	114.3(5)
O(3)-N(3)-N(4)	117.2(7)	O(3)-N(3)-N(2)	113.2(7)
N(4)-N(3)-N(2)	129.5(5)	N(3)-N(4)-C(4A)	113.6(6)
N(4)-C(4A)-C(5)	122.0(6)	N(4)-C(4A)-C(8A)	123.1(6)
C(5)-C(4A)-C(8A)	114.8(5)	C(6)-C(5)-C(4A)	122.3(5)
C(6)-C(5)-N(5)	116.7(7)	C(4A)-C(5)-N(5)	121.0(6)
O(5B)-N(5)-O(5A)	124.8(8)	O(5B)-N(5)-C(5)	119.2(8)
O(5A)-N(5)-C(5)	115.9(8)	C(5)-C(6)-C(7)	119.4(6)
C(8)-C(7)-C(6)	122.2(6)	C(8)-C(7)-N(7)	119.5(6)
C(6)-C(7)-N(7)	118.2(6)	O(7B)-N(7)-O(7A)	123.6(6)
O(7B)-N(7)-C(7)	119.8(6)	O(7A)-N(7)-C(7)	116.5(6)
C(7)-C(8)-C(8A)	117.8(5)	C(8)-C(8A)-N(1)	120.6(5)
C(8)-C(8A)-C(4A)	123.4(5)	N(1)-C(8A)-C(4A)	115.9(5)
O(11)-N(11)-N(12)	116.3(6)	O(11)-N(11)-C(18A)	120.3(7)
N(12)-N(11)-C(18A)	123.4(7)	N(11)-N(12)-N(13)	116.5(6)
O(13)-N(13)-N(14)	119.4(7)	O(13)-N(13)-N(12)	114.1(6)
N(14)-N(13)-N(12)	126.3(6)	N(13)-N(14)-C(14A)	115.1(6)
N(14)-C(14A)-C(18A)	123.6(6)	N(14)-C(14A)-C(15)	120.1(6)
C(18A)-C(14A)-C(15)	116.2(5)	C(16)-C(15)-C(14A)	119.8(6)
C(16)-C(15)-N(15)	118.0(5)	C(14A)-C(15)-N(15)	122.2(6)
O(15B)-N(15)-O(15A)	123.8(7)	O(15B)-N(15)-C(15)	120.1(6)
O(15A)-N(15)-C(15)	116.1(7)	C(15)-C(16)-C(17)	120.5(6)
C(18)-C(17)-C(16)	122.1(6)	C(18)-C(17)-N(17)	119.6(6)
C(16)-C(17)-N(17)	118.2(6)	O(17B)-N(17)-O(17A)	125.9(6)
O(17B)-N(17)-C(17)	117.4(7)	O(17A)-N(17)-C(17)	116.7(6)
C(17)-C(18)-C(18A)	118.0(6)	C(18)-C(18A)-C(14A)	123.3(6)
C(18)-C(18A)-N(11)	121.8(6)	C(14A)-C(18A)-N(11)	114.8(6)

TABLE A-12. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **18**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^*b^*U_{12}]$.

	U11	U22	U33	U23	U13	U12
N(1)	49(3)	56(3)	61(3)	3(3)	11(3)	6(2)
O(1)	65(3)	79(3)	90(3)	-2(3)	17(3)	-30(3)
N(2)	80(3)	62(4)	68(4)	0(3)	17(3)	6(3)
N(3)	111(5)	70(4)	49(4)	0(3)	11(4)	24(4)
O(3)	195(7)	116(5)	64(4)	-18(3)	32(4)	-2(5)
N(4)	94(4)	60(3)	58(4)	-11(3)	-15(3)	9(3)
C(4A)	50(3)	42(3)	55(4)	3(3)	-14(3)	18(3)
C(5)	49(3)	41(3)	71(4)	3(3)	-25(3)	-3(3)
N(5)	88(4)	57(4)	96(5)	16(4)	-36(4)	-23(3)
O(5A)	89(4)	92(4)	219(8)	-12(5)	-21(5)	-46(3)
O(5B)	208(7)	74(4)	91(4)	-6(4)	-40(5)	-51(4)
C(6)	42(3)	52(4)	67(4)	9(3)	-9(3)	-8(3)
C(7)	43(3)	58(4)	54(4)	8(3)	-2(3)	4(3)
N(7)	70(4)	78(4)	58(4)	-5(3)	-1(3)	-1(3)
O(7A)	121(4)	101(4)	75(3)	-26(3)	16(3)	-21(3)
O(7B)	97(4)	168(5)	70(4)	13(4)	34(3)	-33(4)
C(8)	42(3)	44(3)	53(4)	-5(3)	-5(3)	-1(3)
C(8A)	34(2)	40(3)	58(4)	0(3)	-2(3)	0(2)
N(11)	95(5)	55(4)	84(4)	11(4)	-31(4)	2(3)
O(11)	127(5)	82(3)	92(4)	44(3)	-15(4)	1(3)
N(12)	71(4)	78(4)	121(6)	24(4)	-17(4)	8(3)
N(13)	63(4)	74(4)	117(5)	17(4)	-21(4)	5(3)
O(13)	57(3)	119(5)	170(6)	27(5)	-13(4)	6(3)
N(14)	63(3)	72(3)	90(4)	8(3)	-13(3)	0(3)
C(14A)	54(3)	47(3)	62(4)	-3(3)	-17(3)	-5(3)
C(15)	64(4)	42(3)	46(3)	8(3)	-11(3)	-5(3)
N(15)	70(4)	77(4)	77(4)	20(4)	-4(4)	-13(3)
O(15A)	169(6)	80(4)	117(5)	51(4)	27(5)	26(4)
O(15B)	80(3)	178(6)	108(5)	70(5)	25(4)	26(4)
C(16)	59(4)	46(4)	62(4)	1(3)	-11(3)	-3(3)
C(17)	59(3)	44(3)	55(4)	-10(3)	-4(3)	1(3)
N(17)	78(4)	65(3)	74(4)	-8(3)	9(3)	-2(3)
O(17A)	77(3)	102(4)	133(6)	22(4)	10(4)	12(3)
O(17B)	119(4)	99(4)	78(4)	0(3)	36(3)	1(3)
C(18)	77(4)	54(4)	45(3)	-4(3)	4(3)	-6(3)
C(18A)	75(4)	36(3)	56(4)	5(3)	-18(4)	-4(3)

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1 Army Missile Command, Redstone Arsenal (L. Aseoka)
4 Army Ballistic Research Laboratory, Aberdeen Proving Ground
    DRXBR-IBD
        Director (1)
        A. Junasz (1)
        Dr. I. W. May (1)
    AMXBR-TBD, J. J. Rocchio (1)
1 Army Research Office, Research Triangle Park (R. Ghirardeli)
1 Ballistic Missile Defense Advanced Technology Center, Huntsville (D. C. Sayles)
2 Air Force Academy, Colorado Springs (FJSRL/NC, J. S. Wilkes, Jr.)
1 Air Force Wright Laboratory, Armament Drectorate, Eglin Air Force Base (WL/MNF, O. K. Heiney)
1 Headquarters 497 IG/INT, Falls Church (OUWG Chairman)

4 Phillips Laboratory, Edwards Air Force Base
   OL AC PL/LKLR
      B. Goshgarian (1)
      Dr. T. Hawkins (1)
   OL AC PL/RKCP, L. Dee (1)
   Technical Library (1)
1 Advanced Research Projects Agency, Arlington (Dr. R. Loda)
1 Lawrence Livermore National Laboratory, Livermore, CA
      Dr. R. Atkins (1)
      Dr. A. Mitchell (1)
      Dr. P. Pagoria (1)
      Dr. R. Simpson (1)
1 Los Alamos National Laboratory, Los Alamos, NM (Dr. M. Hiskey)
4 Aerojet General Facility, Sacramento, CA
      Department 5400 (1)
      Dr. T. C. Archibald (1)
      Dr. R. Lou (1)
      T. C. Manser (1)
1 Alliant Techsystems, Magna, UT (C. Butcher)
1 Alliant Techsystems, Missile Ordnance and Space Group, Rocket Center, WV (Dr. K. D. Hartman)
1 Analy-Syn Laboratories, Incorporated, Paoli, PA (Dr. V. Keenan)
1 Atlantic Research Corporation, Alexandria, VA (M. King)
4 Atlantic Research Corporation, Gainesville, VA
      G. T. Bowman (1)
      K. Graham (1)
      R. E. Shenton (1)
      B. Wheatley (1)
1 Center for Naval Analyses, Alexandria, VA (Technical Library)
1 Fluorochem, Incorporated, Azusa, CA (Dr. K. Baum)
1 Rockwell International Corporation, Rocketdyne Division, Canoga Park, CA (Dr. J. Weber)
2 SRI International, Menlo Park, CA
      Dr. Bottaro (1)
      Dr. R. Schmitt (1)
2 The Ensign-Bickford Company, Simsbury, CT
      C. N. Kaiser (1)
      Dr. P. F. Meunier (1)
1 The Johns Hopkins University, Chemical Propulsion Information Agency, Columbia, MD (T. Christian)
1 Thikol Corporation/Elkton Division, Elkton, MD (E. Sutton)
1 Thiokol Corporation/Huntsville Division, Huntsville, AL (Dr. W. Graham)
1 Thiokol Corporation/Longhorn Division, Marshall, TX (Dr. D. Dillahay)
2 Thiokol Corporation/Shreveport Division, Shreveport, LA
      L. Estabrook (1)
      Dr. J. West (1)
3 Thiokol Corporation/Utah Division, Brigham City, UT
      D. A. Flanigan (1)
      Dr. J. Hinshaw (1)
      R. Wardle (1)
1 3M Corporation, St. Paul, MN (T. Manzara, Bldg. 236GB)
1 Unidynamics/Phoenix, Incorporated, Phoenix, AZ (Dr. T. W. Fronabarger)
1 United Technologies Corporation, San Jose, CA (CSD Library)